Residual Contamination and Environmental Effects at the Former Vanda Station, Wright Valley, Antarctica.

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Submitted in partial fulfilment for the degree of

Master of Water Resource Management

Waterways Centre for Freshwater Management, University of Canterbury, New Zealand

2015

Abstract

Antarctica is regarded as a pristine environment, free from anthropogenic impacts. However, environmental contamination in areas of human occupation has occurred and can persist long after occupation ceases. Residual contamination of the land on which the former Vanda Station was built, remained following the stations decommissioning and site remediation in 1994. Since then the level of Lake Vanda has risen flooding most of the contaminated site. A re-evaluation was carried out to determine whether the flooding had allowed contaminants to enter the lake itself.

Contamination was not found in the water column of Lake Vanda above the now flooded soils where contaminants had previously been found. Concentrations of trace elements, nutrients and organic compounds measured in the water were all within the natural concentration range in Lake Vanda. Observations of benthic cyanobacteria in affected and control sites indicated slightly enhanced growth at affected sites. Phosphate fertilisation may be contributing to this luxurious growth, and there appears to be no inhibition due to toxic trace elements.

This study identified two fuel spills on the remaining unflooded land near the footprint of the former station. These soils contained elevated total petroleum hydrocarbons (TPH 2400-8900mg/kg), and the trace metals Pb (max 98.16 mg/kg) and Zn (max 158.16 mg/kg). These metal concentrations exceed ANZECC sediment guideline values and TPH exceeds the lowest observed effect concentration for Antarctic mosses. Toxicity characteristic leaching procedure (TCLP) results indicate the potential for Pb and Zn leaching from these soils in both acidic and neutral pH waters.

While similar levels of contamination were found in Vanda Station soils in 1993 and 1997, and have not resulted in obvious adverse effects, the remediation of former work sites in Antarctica is required under The Madrid Protocol. The opportunity for minor remediation of these exposed soils, and the collection of litter and painted rocks exists. This process is recommended to remove sources of contaminants to Lake Vanda permanently in keeping with The Madrid Protocol.

Acknowledgements

Many people have helped me throughout the past two years to get me to this point. I would like to thank Joshua Gibson for assisting me in building sampling equipment, Scott Base for logistical support in Antarctica, Neil Foley for field assistance and NIWA for facilitating the return of samples to New Zealand.

Thank you to Hill Laboratories, Cawthron Institute, the UC Chemistry Department, John Revell and Emma MacKenzie for sample analysis and assistance with analysis. Thank you to all the Waterways students who I have annoyed for help or information, or just an excuse to have a beer for lunch. Very big thank you to Suellen Knopick, your infectious laugh makes every day in the Waterways office a great day to be working. You are an absolutely amazing person for us students to have around!

Thank you to Dr Ed Butler at Antarctica New Zealand and the Waterways Centre for funding, without money this would have been, well, impossible.

Special thank you to Vanessa Gopperth for proofreading my work, not throwing too many staplers at me, and being a great help in all matters! You are a literal rock star!

Thank you to my mum and dad for helping and putting up with me over the past two years, and to Bailey for not being annoyed when I'm tired, grumpy, or just talking endlessly about university.

And finally, thank you to my three supervisors. Jenny Webster-Brown, Sally Gaw, and Ian Hawes, you three have been an invaluable source of help and information, sorry for annoying you so much!

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Abbreviations

All elements are represented by their symbol throughout.

ANZECC	Australia New Zealand Environmental Conservation Council
ATS	Antarctic Treaty System
CCME	Canadian Council of Ministers of the Environment
CDT	Conductivity, depth, temperature scanner
CG	Control Gully sampling site
CGS	Control Gully soil sampling site
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
DRP	Dissolved reactive phosphorus
DVDP	Dry Valleys drilling project
GCMS	Gas chromatography mass spectrometry
GPS	Global positioning system
GW	Sampling site code for Greywater Gully sites
HP	Sampling site code including helicopter pads or fuel spill site on land
HPIC	High pressure ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
IEE	Initial environmental evaluation
IGY	International Geophysical Year 1957-1958
LOEC	Lowest observed effect concentration
Madrid Protocol	The Protocol for Environmental Protection to the Antarctic Treaty
McMLTER	McMurdo Dry Valleys long term ecological research project
MPI	Ministry of Primary Industries

NGS	Next generation sequencing
NIWA	National Institute of Water and Atmospheric Research
OS	Off station sampling site
PAH	Polycyclic aromatic hydrocarbon
PC1/PC2	Physical containment facility
TC	Total carbon
TCLP	Toxicity characteristic leaching procedure
TOC	Total organic carbon
TPH	Total petroleum hydrocarbons
USAP	United States Antarctic Program
VBG	Vanda Back Gully sampling site
VOC	Volatile organic compound

Chapter 1 - Introduction

1.1 Human Presence in Antarctica

Antarctica is a continent of superlatives; it is the most remote, cold, windy and dry continent on Earth (Bargagli, 2008). Although the driest, Antarctica is home to the largest reserve of fresh water, locked within the East and West Antarctic ice sheets (Bargagli, 2006; Caroli, Cescon, & Walton, 2001). Aided by its remote and inhospitable nature, the Antarctic environment is considered the most pristine on Earth (Tin, Liggett, Maher, & Lamers, 2013). Despite this, Antarctica is subject to increasing human presence and associated environmental impacts at both a continental and local scale (Bargagli, 2008).

Antarctica has attracted scientists from around the world for multidisciplinary research across the continent. Of particular research interest are the effects of global and regional environmental change on the diverse environments and ecological systems (Bargagli, 2006). Seventy stations and research bases have been established by thirty different countries (Bastmeijer, 2003). The majority of these research stations were commissioned after the International Geophysical Year (IGY) 1958-1959 (Tin *et al.*, 2013). The stations are all subject to the Antarctic Treaty, and are occupied by 4000-5000 people during the austral summer, and up to 1000 people during the austral winter (Bargagli, 2008). The operation of these stations, field camps, and scientific activities create a number of environmental pressures that can have extensive and long lasting impacts (Benninghoff & Bonner, 1985).

The Antarctic continent and marine environs are subject to additional pressures associated with tourism and fishing. Visitor numbers to the Antarctic Treaty System area (ATS area), south of 60^{o}S latitude, reached 60,000 people in the austral summer 2006/07 (Gröndahl, Sidenmark, & Thomsen,

2009). This influx of visitors, particularly to the sensitive marine environments and ice-free land, increases the risk of introducing biological and chemical pollutants (Bargagli, 2006; Gröndahl *et al.*, 2009).

1.2 The Antarctic Treaty System

The Antarctic Treaty, and supporting protocols within the ATS, regulate international interests and relations of contracting countries within Antarctica (Beeby, 1972).

Antarctica has been declared a continent dedicated to peaceful purposes and scientific research under the Protocol for Environmental Protection (hereby referred to as The Madrid Protocol) as part of the ATS (Antarctic Treaty, 1959; Madrid Protocol, 1991). The ATS arose during The Cold War as a measure to demilitarise the continent (Myhre, 1986) and freeze claims on territories. Provisions in the ATS include the conservation of marine life, the banning of nuclear waste disposal, and the prohibition of mining apply to the continent and all environs south of 60^{o}S latitude excluding open sea water (Article VI) (Antarctic Treaty, 1959). Contracting countries individually passed legislation governing their activities in Antarctica in line with the ATS (Myhre, 1986).

The ATS evolved to advocate for scientific enquiry and collaboration between contracting parties (Beeby, 1972; Myhre, 1986). The Treaty, although successful in promoting scientific research, failed to provide comprehensive regulation for the protection of the Antarctic environment (Antarctic Treaty, 1959; Beeby, 1972). With no clear protocol on environmental protection, Antarctica became vulnerable to environmental degradation as human presence increased (Bargagli, 2008). Legal tools introduced into the ATS since 1964 addressed environmental issues, however it was not until The Madrid Protocol (1991) was signed that there was comprehensive environmental protection for the continent (Bastmeijer, 2003; Madrid Protocol, 1991).The Madrid Protocol was signed in 1991 and ratified in 1998, with New Zealand adopting the protocol by passing the Antarctica (Environmental

Protection) Act 1994 (Madrid Protocol, 1991; Waterhouse, 1997). The requirement for contracting parties to clean up all past and present work sites was included in The Madrid Protocol. This requirement applies unless the remediation efforts adversely affect the environment more than if contaminants remained.

1.3 Environmental Pressures and Effects

Prior to the signing and implementation of The Madrid Protocol, biological and chemical contamination occurred at areas of concentrated human activity (Waterhouse, 1997). This contamination resulted from the disposal of wastes onto land and marine environments, burying or burning of waste, and the physical disruption of the environment including earthworks (Aronson, Thatje, McClintock, & Hughes, 2011). The main anthropogenic pressures and impacts in Antarctica include climate change, marine pressures and terrestrial pressures.

Climate change is a multifaceted pressure; of particular concern is the warming of the sea and atmosphere, and a change in the dynamics of both sea and land ice. Climate change constitutes a long-term threat to the ATS area. Some ice shelves have already collapsed, specifically the Larsson-B ice shelf, and some glaciers and ice shelves are thinning (Turner *et al.*, 2009). Climate change also has wide-spread effects on populations of penguins and marine birds, with breeding and range being affected (Barbraud & Weimerskirch, 2001).

Fishing, particularly the over exploitation of specific lower trophic species, has had an observed effect throughout the food chain (Constable *et al.*, 2000). Marine and coastal pollution is another common pressure associated with fishing and tourism operations in the ATS area (Müller, Lundmark, & Lemelin, 2012). Such pressures consist of hydrocarbon pollutants resulting from fuel spills, hydraulics and engine wastes, biological, nutrient and organic pollutants originating from the

disposal of effluent, rubbish from fishing and tourism parties, and the disturbance of populations of nesting birds from landing parties (Müller *et al.*, 2012).

Permanently manned stations have been operated in the ATS area since the IGY. Prior to the signing of The Madrid Protocol, many stations exerted pressures on the surrounding land and marine environments (Bargagli, 2008). Consideration of environmental effects originating from the operation of these stations was not as robust as today (Waterhouse, 1997). As a result, stations contaminated the surrounding land and sea through poor environmental protocol and management. Common pollutants released included leaking and spilled oils, fuels and petroleum wastes, disposal of treated and untreated wastewater and greywater to land and sea, and the burning, burial or inappropriate disposal of potentially toxic or contaminating wastes (Kennicutt II *et al.*, 2010; Tin *et al.*, 2009; Williams, 2012).

The most common contaminants in soils and waters surrounding former stations are trace metals, hydrocarbons and pathogens (Aronson *et al.*, 2011; Santos *et al.*, 2005). Frequently detected trace metal contaminants include Pb, Zn, Ni, Cu and Cr (Claridge *et al.*, 1995; Sheppard, Claridge, & Campbell, 2000). These trace metals released tend to persist as there is little terrestrial biological activity and physical weathering such as meltwater runoff to disperse them (Santos *et al.*, 2005). Impacts from trace metals are generally limited due to the lack of bioavailability and mobility in the terrestrial environment and the effects are confined to marine and freshwater environments (Aronson *et al.*, 2011).

A specific example of anthropogenic environmental contamination is the minor and continuous effects that occurred during the operation of New Zealand's Vanda Station in the Wright Valley (Waterhouse, 1997). Here, discrete diesel and mogas spills, along with frequent disposal of

greywater to land occurred over the 25 years of occupation (Sheppard, Campbell, Claridge, & Deely, 1994; Waterhouse, 1997; Webster, Webster, Nelson, & Waterhouse, 2003).

Other stations operated around the continent also have legacy contamination issues. Casey Station (operated by Australia) and McMurdo Station (operated by the United States) has to a larger extent legacy issues of soil and water contamination (Snape *et al.*, 2001; Stark, Snape, & Riddle, 2006). Major clean-up programs and implementation of stricter protocol have since occurred. Following the ratification of the Madrid Protocol the focus has shifted to remediation of sites and the prevention of issues from arising.

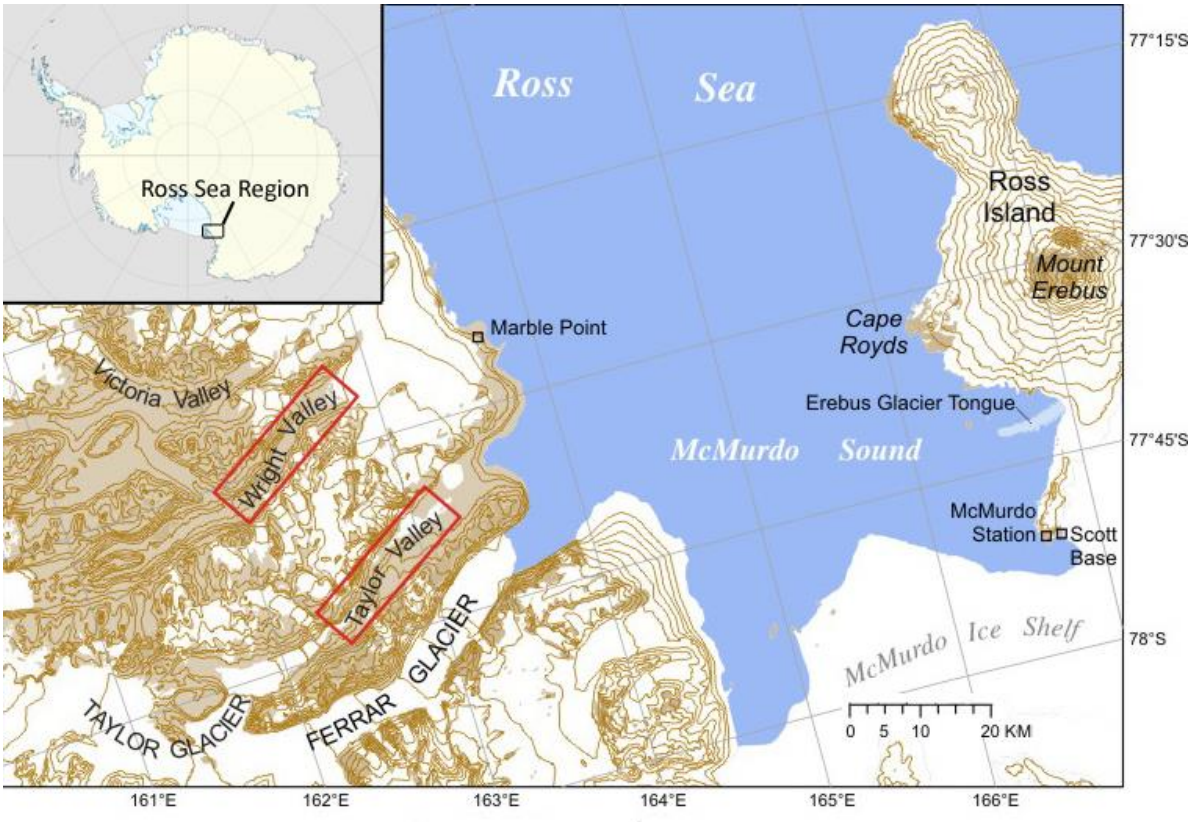


Figure 1 - Ross Sea region and McMurdo Dry Valleys. Inset: Ross Sea Region in relation to Antarctica (USGS, 2010).

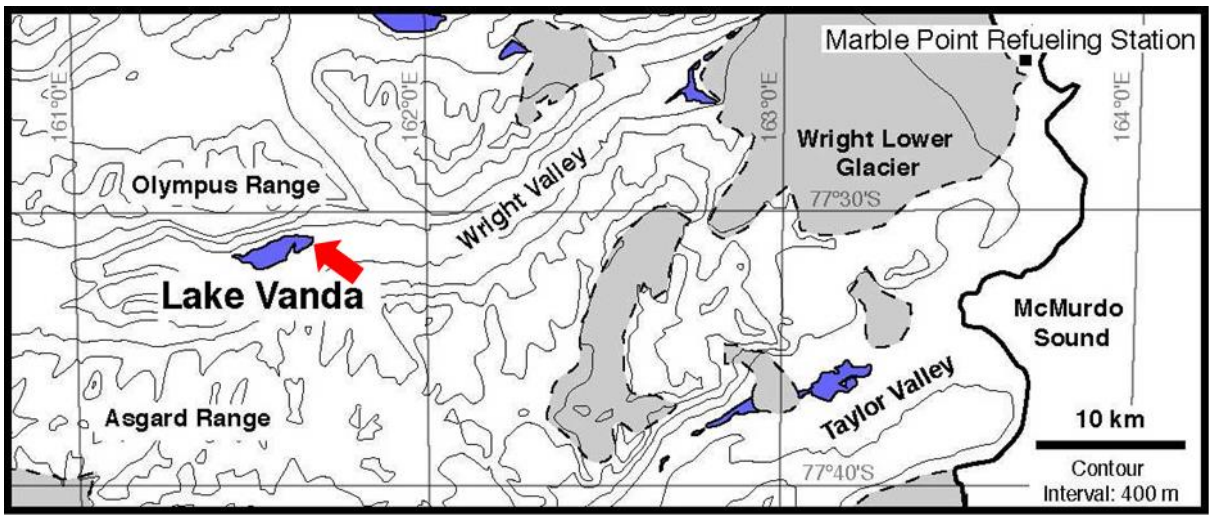


Figure 2 - Wright Valley, McMurdo Dry Valleys. The former Vanda Station was located at eastern end of Lake Vanda (arrow).

1.4 Lake Vanda

Lake Vanda is an ice-covered, ultra-oligotrophic, meromictic (stratified, non-mixing), endorheic (closed basin) lake in the Wright Valley, McMurdo Dry Valleys, Antarctica (Figure 1, Figure 2) (Canfield & Green, 1985). The lake occupies a glacial basin in the Wright Valley, bordered by the steep Asgard and Olympus ranges. Lake Vanda has been intensely studied since its discovery, and maintains a complete record of hydrological observations since 1968 (Chinn, 1993).

Lake Vanda is approximately 8km long, 2km wide as of 1998 (Spigel & Priscu, 1998), substantially larger than the 5.6km long and 1.5km wide surveyed in 1963 (Angino & Armitage, 1963). Lake Vanda is approximately 75m deep (2010), and is perennially covered by transparent ice ranging 2-4m thick (Green & Lyons, 2009; Hawes *et al.*, 2013). This ice cover occasionally melts during the height of summer to form an open water moat in the littoral (close to shore) zone (Spigel & Priscu, 1998).

Lake Vanda's evolution through the late Pleistocene and Holocene saw considerable fluctuations in lake level caused by variations in regional climate (Chinn, 1993; Green & Canfield, 1984). A theorised former "Great Lake Vanda" underwent considerable change, where a slow evaporative event

reduced the lake to a shallow hypersaline pond (Hall, Denton, & Overturf, 2001). The remnants of this hypersaline pond constitute the deep brines found in Lake Vanda today (Chinn, 1993). Recent inflows of relatively fresh water from the Onyx River lie above this hypersaline base, creating the meromictic stratification currently observed (Green & Canfield, 1984; Green *et al.*, 2005).

The Onyx River, the major contributing source of water into Lake Vanda, is Antarctica's longest river (Green *et al.*, 2005). When active, it flows for 28km from the proglacial Lake Brownworth at the Lower Wright Glacier (Green & Canfield, 1984). The Onyx River intermittently flows for 6-8 weeks, generally starting mid-December (Green & Canfield, 1984). Seasonal inflows are highly variable however, where total input volume can range from $0m^3$ (1977/78), to $15x10^6m^3$ (1970/71) per summer season (Chinn, 1993). Variation in flow is caused by seasonal weather patterns in McMurdo Sound resulting in irregular melt on the Lower Wright Glacier and Lake Brownworth (Chinn, 1993; Waterhouse, 1997). Climate projections anticipate an increase in average temperature in McMurdo Sound (Turner *et al.*, 2009). This anticipated increase in temperature could correspond with increasing melt on the Lower Wright Glacier, earlier melt and release of water from Lake Brownworth and prolonged flow in the Onyx River (Castendyk, 2014).

Lake Vanda loses water through ablation only as there is no physical outlet (Priscu & Foreman, 2009). The ablation rate is relatively constant, with a calculated average 326mm $year^{-1}$ (standard deviation 121mm), major changes to the water balance equilibrium is due to variable inflow (Chinn, 1993). Since 1968/69 when systematic recording began, the lake level has risen (Figure 3) from 81.5masl (1968/69), 89.0masl (1988/89) to 94.3masl (2012/13) (Chinn, 1993; Green & Lyons, 2009; McMLTER, 2015). Annual change in lake level is not consistent and occasionally negative, on three occasions annual rise exceeded 1000mm: 1970/71 - 2106mm, 1984/85 - 1095mm and 1986/87 - 1400mm (Chinn, 1993).

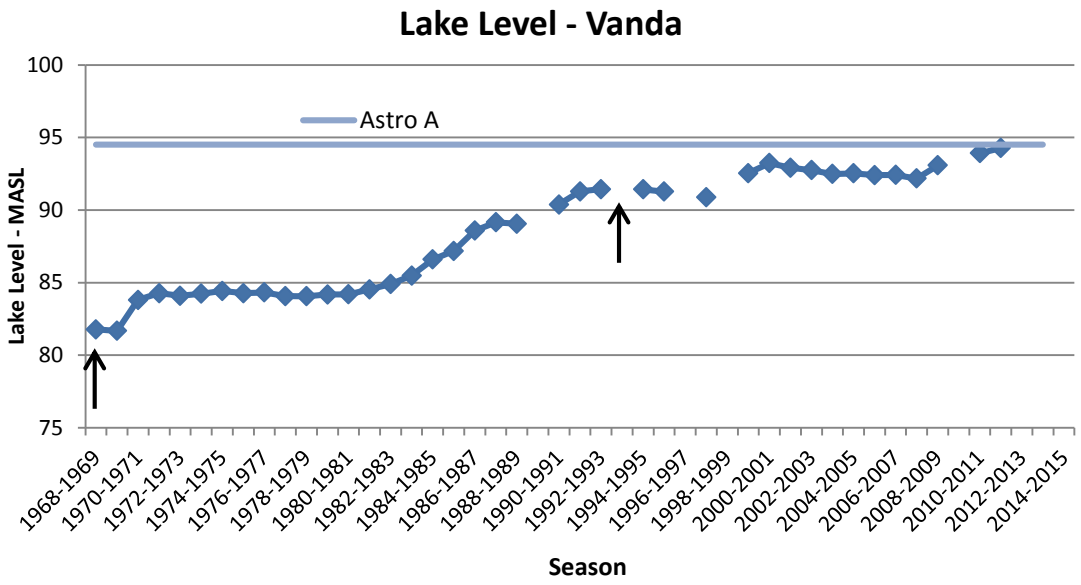


Figure 3 - Lake Vanda level rise since 1968 relative to Astro "A" survey point. Data series 1968-1989 (Chinn, 1993), 1990-2014 (McMLTER, 2015). The two arrows refer to the commissioning and decommissioning of the station.

Lake Vanda has two distinct layers in a meromictic system (Green & Lyons, 2009). The lake exhibits strong solute and temperature stratification with very little mixing between layers (Green & Lyons, 2009; Green & Canfield, 1984). The upper layer and littoral waters (0-45m) are characterised by fresh, highly oxygenated water with a high pH. This layer is mixed by a slow convective cell and remains relatively cool with temperatures that range from 4° C below the ice surface to 7° C above the thermo/chemocline (McMLTER, 2015). Below the thermocline the temperature rises rapidly to 22°C (McMLTER, 2015). The deep saline layer is warmed by trapped solar energy and is held stable below the chemocline (Green & Lyons, 2009; Priscu & Foreman, 2009).

1.4.1 Microbial Communities

Lake Vanda's ecosystem is dominated by primary producers with very few higher trophic species (Hawes *et al.*, 2013). Of particularly importance to Lake Vanda's ecosystem is benthic cyanobacterial species forming thick laminar mats inhabited by *Lyngbya, Leptolyngbya*, *Oscillatoria* and *Phormidium* species (Hawes *et al.*, 2013; Quesada, Fernandez-Valiente, Hawes, & Howard-Williams, 2008). Pennate diatoms are present in these mats in lower abundance with species of *Diademis, Achnanthes, Navicula, Muelleria, Luticola and Stauroneis* (Quesada *et al.*, 2008). In recently flooded

areas, benthic cyanobacterial mats can accumulate up to ~0.18µg chlorophyll-a cm^{-2} $year^{-1}$ (Hawes *et al.*, 2013) or 1.2 mg carbon cm^{-2} $year^{-1}$ (Hawes *et al.*, 2001) with the addition of one laminar (~0.3mm) per year. With the lack of higher trophic species, accumulation of primary biomass can occur undisrupted; however, growth and biomass accumulation is very responsive to environmental change (Hawes, Smith, & Sutherland, 1999; Hawes *et al.*, 2013; Quesada *et al.*, 2008).

Phytoplankton growth in Lake Vanda is phosphorus and light limited, contributing to low total primary production in its upper water and benthic environs (Howard-Williams, Hawes, & Schwarz, 1997). Cyanobacterial species dominate waters where nutrient concentration is low, whereas species dominance shifts to a higher proportion of diatom species when enriched with nutrients (Hawes *et al.*, 1999). Microcosm experiments undertaken by Hawes *et al* (1999) indicate that nutrient enrichment as found in Greywater Gully sediments can increase growth rate, final biomass yield, and change species composition.

1.5 Vanda Station - A New Zealand Outpost

New Zealand has operated two bases in Antarctica, Scott Base (77° 51' S, 166° 46' E) from 1957-present, and Vanda Station (77° 31’ S, 161° 40’ E) from 1968-1992 (Harrowfield, 1999). Scott Base, located on Ross Island, operates as New Zealand’s year round staging post for research in Antarctica (Figure 1). Scott Base provides logistical and field support, maintains NZ’s permanent presence in its territorial claim, and provides joint science support services with the United States Antarctic Program’s (USAP) McMurdo Station (Harrowfield, 1997). Vanda Station (Figure 4) was located in the Wright Valley (Figure 2) on the Antarctic mainland, in the McMurdo Dry Valleys, Southern Victoria Land. Once completed, Vanda Station was located 140m south-east of Lake Vanda, 110m from the Onyx River and at 9m above lake level. The idea for a mainland station arose following an increase in scientific interest in the McMurdo Dry Valleys (Harrowfield, 1999). Scientific programs in the Wright Valley commenced in 1958 utilising USAP air support. The following 10 years saw further

development of these programs and a need for a local support station (Harrowfield, 1999). The construction of Vanda Station commenced in 1967. Materials were air-dropped onto Lake Vanda via C130 Hercules, and later bought in via tractor in 1968/69. The majority of construction occurred in the summer of 1968, and on the 20th December 1968 scientific programmes got underway at Vanda Station (Harrowfield, 1999). The station, at its peak, consisted of seven buildings and huts, paths, four helicopter pads, meteorological equipment, masts and antennae, and vehicles (Harrowfield, 1999).Vanda Station hosted research across numerous scientific disciplines, including meteorology, geology, glaciology, soil science, lake limnology, seismology, freshwater chemistry, biology, ecology, physics and studies into the ionosphere (Harrowfield, 1999). Lake Vanda also hosted the 1973/74 Dry Valleys Drilling Project (DVDP), seeing two deep cores of lake sediments extracted. Vanda Station provided essential support for the DVDP project (Torii, 1981). The station also gained a reputation as hospitable waystation for transient Antarctic research and aircraft personnel (Sheppard *et al.*, 1994). The station over its 25 years of operation received approximately 10,000 visitors, averaging 400 per year. The majority of short duration visits were from Scott Base staff, distinguished visitors, aircraft crew, and entourage.

Figure 4 - Vanda Station in 1990/1991 season looking west towards the Asgard Ranges. Photo credit Paul Brody.

1.5.1 Environmental Management at Vanda Station

At Vanda Station, there was frequent greywater disposal, fuel spills and leaks, and unregulated use of vehicles on the lake and valley floor (Sheppard *et al.*, 1994). All of these practices posed risks to the environment, often involving the release of contaminants. Vanda Station operated from 1968-1992. In 1991, station protocols to account for waste management were enacted. Throughout Vanda Station's decommissioning up until 1994, contaminant release prevention was of high priority (Hayward, Macfarlane, Keys, & Campbell, 1994; Waterhouse, 1997).

The most comprehensive assessment of environmental management procedures at Vanda Station was a survey of past station leaders (Sheppard *et al.*, 1994). Results from Sheppard *et al* (1994) indicated the sources of contaminants and the locations to consider in subsequent environmental impact studies (Sheppard, Campbell, Claridge, & Deely, 1993; Sheppard *et al.*, 1994). The survey conclusions documented 25 years of environmental disturbance at Vanda Station. This initial survey of Vanda Station Leaders indicated a conscientious effort to avoid major environmental contamination, however, without clear protocol, minor environmental contamination occurred. The management procedures regarding waste disposal and environmental protection were documented. The accuracy of the survey was probably compromised however, due to the anecdotal nature of responses spanning a 25-year period, and a participation rate of only 63%.

1.5.2 Survey Results of Past Leaders

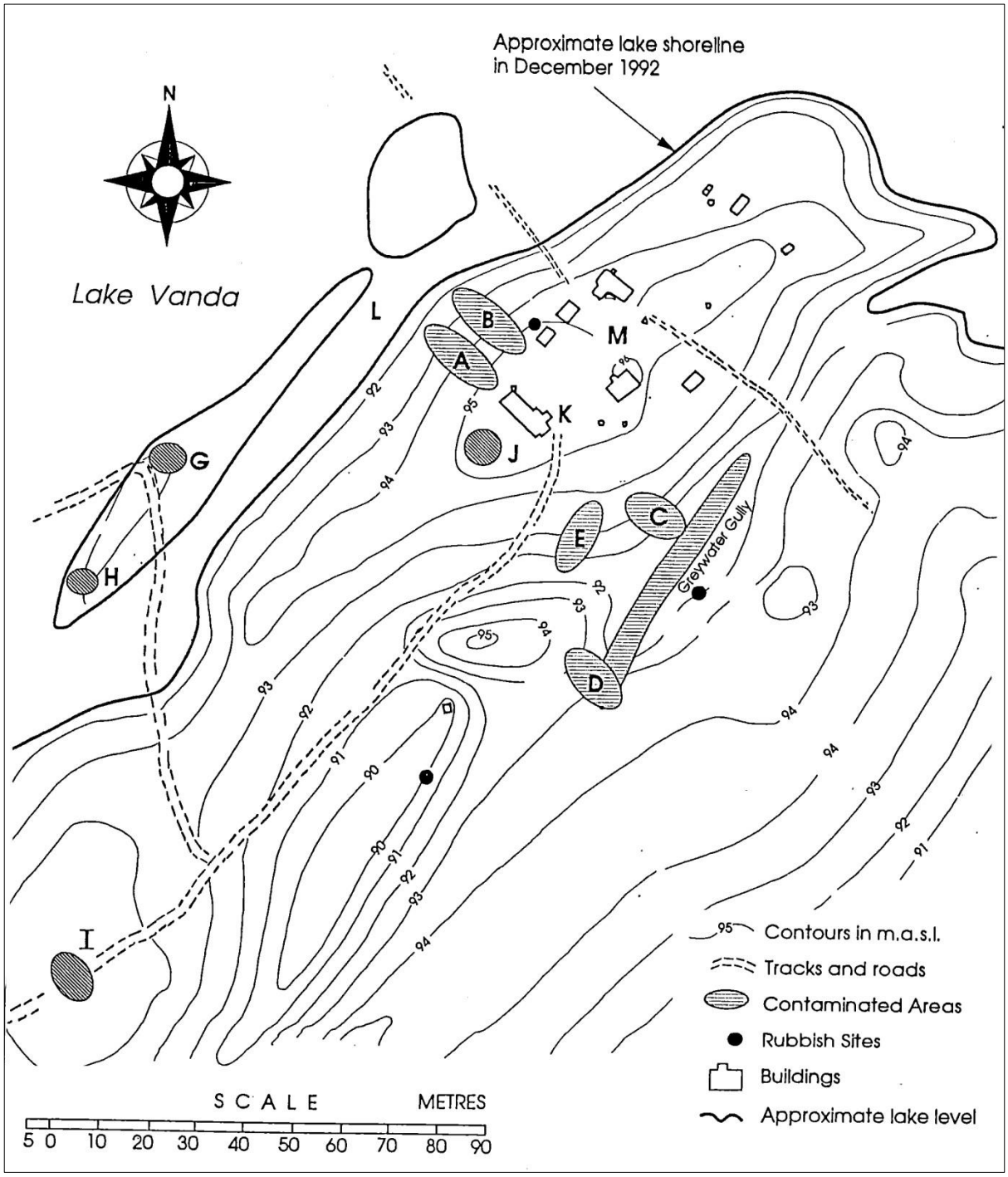


Figure 5 - Locations of spills and disposed contaminants at Vanda Station (sites A-M) as identified by survey responses (Sheppard et al., 1994). Sites referred to in the following section are A-M in this figure.

The survey of past Vanda Station Leaders, undertaken by Sheppard *et al* (1994), indicated that disposal of greywater generated at Vanda Station occurred in Greywater Gully. Greywater was collected and disposed of daily at sites C and D (Figure 5). This greywater contained contaminants including trace metals, phosphates, food oils/fats and other organic compounds (Sheppard *et al.*, 1994). This practice commenced from Vanda Station's opening, and continued until the 1992/93 season when a collection barrel was installed. Subsequently, wastes were flown back to Scott Base for appropriate disposal. Infrequently, photographic solvents containing high concentrations of Ag were disposed with this greywater. Greywater was the main source of contaminants from Vanda Station, with an estimated rate of greywater disposal of 30l/day in 1983/84 and 80l/day in 1986/87. Greywater disposal sites are marked A, B, C, and D in Figure 5. Locations C and D were the most frequently used over the longest time period, sites A and B were very infrequently used.

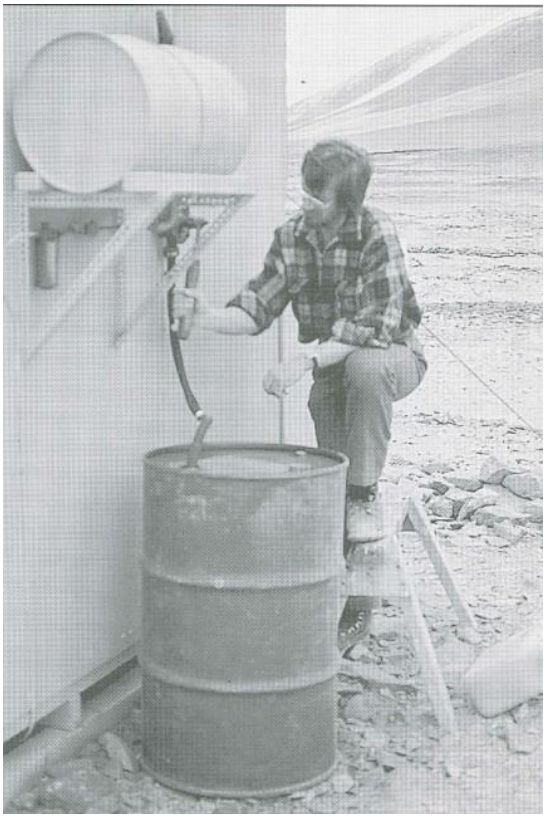


Figure 6 - Refuelling drum at the former Vanda Station. Note the lack of fuel bund or any spill containment measures (Harrowfield, 1999).

Hydrocarbon contamination of soils occurred due to poor management and accidental spillages rather than deliberate disposal. Current standard procedures for refuelling, storage, and movement of fuels, and the use of fuel bunds and spill kits were uncommon (Antarctica NZ, 2014). As a result, diesel fuel was frequently spilled onto soil during transfer or leaked from drums in storage (Figure 6). Individual spills of up to 60L were recalled (Sheppard *et al.*, 1994). Poor refuelling technique led to inevitable spills, although they were usually small quantities (Aislabie *et al.*, 1999; Sheppard *et al.*, 1994). Sites of petroleum contamination identified in this survey include the helicopter pads (G, H, I, J), refuelling site (K) and site E (Figure 5). Site E showed the most obvious contamination during Sheppard et al's (1994) study as the spill was quite recent.

Another source of contamination with potentially high trace metal concentrations, albeit in small quantities, was the disposal of battery acid onto land (Sheppard *et al.*, 1994). This practice, now prohibited, is reported to have occurred on two occasions during the 1974/75 and 1979/80 seasons. Vanda Station's power was generated by a wind turbine with storage provided by lead-acid battery banks (Harrowfield, 1999). Acid disposal reduced the weight of batteries prior to removal; the quantities disposed of, however, were small.

1.5.3 Decommissioning, AEE and Remediation at Vanda Station

Lake Vanda rose 8m between the time of construction and 1989 (Chinn, 1993). During Vanda Station's latter period of occupation, the lake threatened to inundate the station. This risk, coupled with changes in the focus of New Zealand's scientific research program, led to the decision to decommission the station (Harrowfield, 1999; Sheppard *et al.*, 1994; Waterhouse, 1997). The process of decommissioning commenced in the austral summer of 1993/94, with planning and preliminary work carried out. Decommissioning processes and environmental management procedures were documented in the Initial Environmental Evaluation (IEE) (Hayward *et al.*, 1994).

Throughout the decommissioning process, there was an emphasis on removing the risk of contaminants reaching Lake Vanda (Waterhouse, 1997). The main objectives in decommissioning Vanda Station, as stated in the IEE were:

- "To ensure that in the event of the waters of Lake Vanda inundating the Station, there will be an absolute minimum of human induced environmental change to the lake system,
- To ensure that if change is unavoidable, the nature of change is understood and documented,
- To submit proposals for protecting Lake Vanda to national and international review." (Hayward *et al.*, 1994)

The decommissioning process was extensive (Hayward *et al.*, 1994; Waterhouse, 1997). This process included the removal of all manmade structures, the identification and remediation of the most contaminated sites, the identification of potential hazards to the lakes scientific values, and the restoration of surfaces to as natural form as possible. Approximately five tons of the most heavily affected soil was removed immediately. These soils contained visible quantities of contaminants including poly-phosphates, oil residues, animal fats and oils. Further remediation of the site continued for two years (Waterhouse, 1997).

The removal of a total of approximately 15 tonnes of contaminated soil and rock that occurred throughout the remediation process, was transported and deposited at Scott Base (Waterhouse, 1997). This material contained painted marker rocks, hydrocarbon contaminated soil from helipads and refuelling sites, greywater contaminated soil (8m x 4m x 150mm) from Greywater Gully, and other obviously contaminated soil including paint chips, and wood splinters. The remediation process also aimed to restore the site to as natural a state as possible. This included reworking

tracks, moving rocks to a natural state, dismantling cairns and walls and repositioning unnatural looking linear features defined by banks or rocks (Waterhouse, 1997).

During and following the decommissioning process, a number of investigations were undertaken to determine the degree of phosphate and trace metal contamination in the soils of Vanda Station (Sheppard *et al.*, 1993; Sheppard *et al.*, 1994). Monitoring of hydrocarbon contamination and residual contamination followed soon after the decommissioning of Vanda Station (Aislabie *et al.*, 1999; Webster-Brown & Webster, 2007; Webster *et al.*, 2003).

1.6 Residual contamination at the former Vanda Station Site

Following the decommissioning and remediation process, monitoring of potential impacts and the effectiveness of remediation began (Aislabie *et al.*, 1999; Hawes *et al.*, 1999; Sheppard *et al.*, 1993; Sheppard *et al.*, 1994; Webster-Brown & Webster, 2007; Webster *et al.*, 2003). Despite the extensive remediation efforts, discrete pockets of soil and suprapermafrost fluid[1] contamination remained, particularly in the upper reaches of Greywater Gully (Webster *et al.*, 2003).

The nature, mobility and potential environmental effects of contaminants remaining in the vicinity of the former Vanda Station have been investigated prior to lake inundation (Hawes *et al.*, 1999; Webster *et al.*, 2003). These studies concluded a limited potential for release of contaminants to Lake Vanda unless the lake floods affected soil. Greywater gully has subsequently been flooded (Figure 3 Figure 8), with lake waters nearing the survey point 'Astro A' at 94.5m (above sea level) at the time of sampling in this study (Figure 7). Now with Greywater Gully and the helicopter pads

[1] Thin layer of saline water overlying the permafrost layer approximately 60cm below soil surface.

under water, the focus of research at Vanda must shift to the release of contaminants to the Lake's water and any environmental effects.

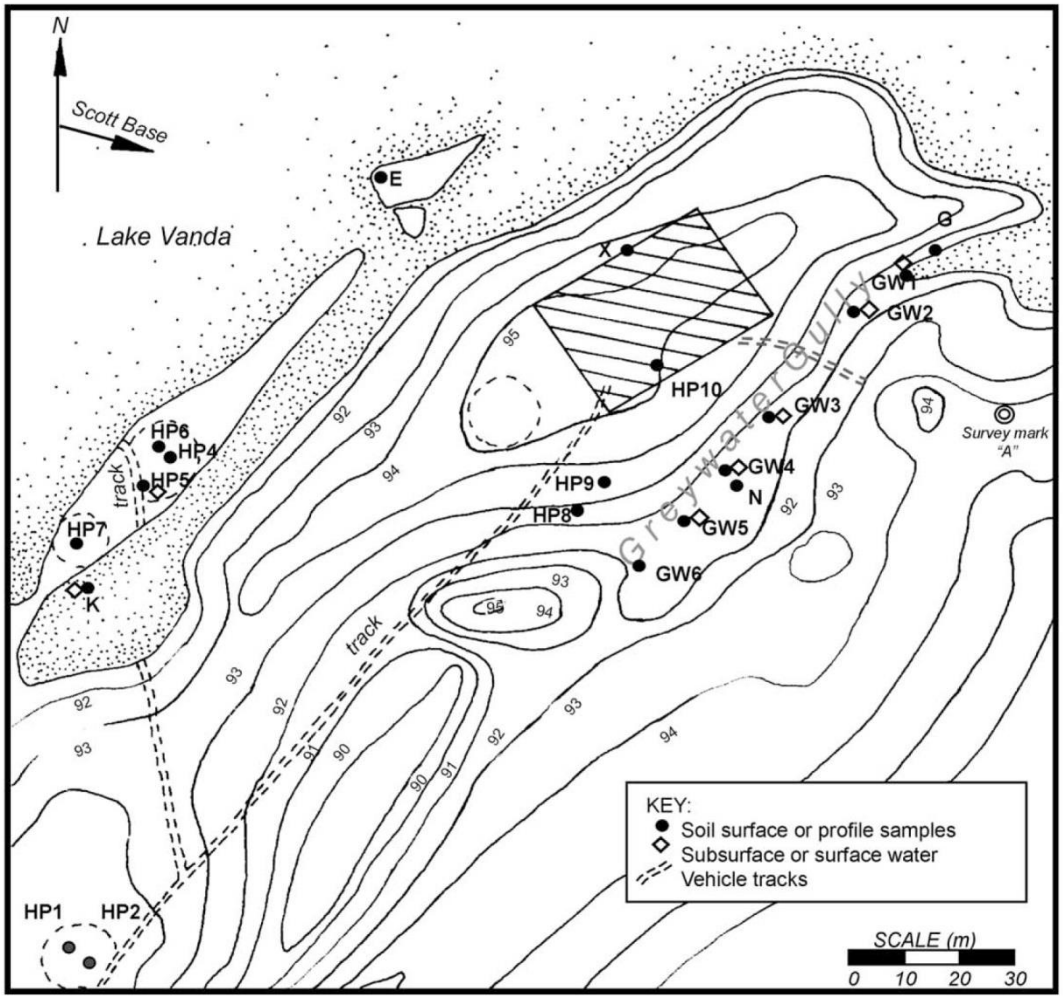


Figure 7 - Sampling map from Webster *et al* (2003) for the former Vanda Station site and Greywater Gully. Note that control sites are not within this frame.

1.6.1 Trace Element Contamination

Studies into trace metal contamination at the former Vanda Station site include investigations into the concentrations in soil and suprapermafrost fluids (Sheppard *et al.*, 1994; Webster *et al.*, 2003), and interaction with cyanobacteria (Hawes *et al.*, 1999; Webster-Brown & Webster, 2007). Trace metals naturally occur in Lake Vanda from inputs such as the Onyx River and groundwater (Green,

Canfield, Lee, & Jones, 1986; Green *et al.*, 2004). The dynamics and speciation of metals in Lake Vanda waters have been extensively investigated, for example (Green, Ferdelman, & Canfield, 1989; Green *et al.*, 2004; Webster, 1994).

Results from Webster *et al* (2003) showed elevated trace element concentrations in the soil profile at sites within the former Station footprint and in Greywater Gully compared with five different control sites. Elevated elements included Pb, Cd, Ag and Zn. Hawes *et al* (1999) also indicate elevated soil concentrations of Ag, Cd, Cu and Pb in Greywater Gully at the confluence with Lake Vanda (approximately GW2 from Figure 7). Results from Webster *et al* (2003) were the most comprehensive study of residual contamination at Vanda Station. These results will be detailed where necessary alongside the discussion of results from this study. They also observed elevated trace metal concentrations in the suprapermafrost fluids where concentrations of Cd, Pb, Zn, Cu, Co, and Ni were above background concentrations at sites GW2, GW3, GW4, GW5 and HP5. There was a distinct increasing trend in the suprapermafrost fluid trace metal concentrations from the lower sites (GW2) to the higher sites (GW4/5) in Greywater Gully where the majority of greywater was disposed. There was no evidence however, of active fluid movement down Greywater Gully towards the lake in 1996 (Webster *et al.*, 2003).

1.6.2 Hydrocarbon Contamination

In 1997 hydrocarbon contaminants, measured as total petroleum hydrocarbons (TPH), were evident at significantly elevated levels in soil profiles HP1 (570-2040mg/kg) and HP10 (450-3140mg/kg) (Figure 7) (Webster *et al.*, 2003). These sites represented the main helicopter pad and adjacent to the main bunk room respectively. Site E (Figure 5), described in Sheppard *et al* (1994) as containing a recent fuel spill, was analysed in Webster *et al* (2003). This site later renamed HP8 and HP9 (Figure 7) contained surface TPH concentrations of 2240mg/kg and 4190mg/kg respectively (Webster *et al.*,

2003). TPH was analysed at a control site (site B) with levels below the detection limit for the test at <2mg/kg (Webster *et al.*, 2003). Webster *et al* (2003) also identified measurable concentrations of naphthalene (34-47µg L^{-1}), acenaphthene (0.54-0.78µg L^{-1}), fluorene (0.89-1.38µg L^{-1}) and phenanthrene (0.14-0.23µg L^{-1}) in acetic acid leachates of soils from site HP10.

Aislabie *et al* (1999) identified polycyclic aromatic hydrocarbons (PAH) concentrations in a fuel spill (unspecified exact location) at the former Vanda Station with concentrations of naphthalene (244µg kg^{-1}), acenaphthene (69µg kg^{-1}), fluorene (286µg kg^{-1}), phenanthrene (1052µg kg^{-1}) and total 16 PAH's (3398µg kg^{-1}).

1.6.3 Nutrient Contamination

Elevated concentrations of Dissolved Reactive Phosphorus (DRP) were measured in suprapermafrost fluids within Greywater Gully at locations GW4, GW5 and GW6 (Webster *et al.*, 2003). In contrast, the nitrate concentrations were low in the most affected sites (GW3, GW4, and GW5). Hawes *et al* (1999) also noted this trend in leachable nutrients, where Greywater Gully samples contained notably higher concentrations of DRP to controls and lower nitrate to controls. Each site had organic matter contents of 1.08% and 0.34% respectively. This anomaly was likely due to enhanced cyanobacterial growth and nitrate uptake bought on by the addition of DRP and organic matter from greywater (Hawes *et al.*, 1999).

Microcosm experiments on contaminated Greywater Gully soils indicated enhanced growth and higher final biomass yield measured as chlorophyll-a compared to uncontaminated soils (Hawes *et al.*, 1999). Any inhibitory effect from trace elements in the sediments were negligible (Hawes *et al.*, 1999).

1.6.4 Release of contaminants

Webster *et al* (2003) indicated the potential for contaminant release from soil into Lake Vanda. The main mechanism for contaminant transfer was determined to be from sediment release due to rising lake waters. They conducted an acidic leaching procedure, which revealed elevated concentrations of Ni, Cd, Cu and Zn from HP10 soils in the acidic leachate. These results do not replicate the natural leaching regime of Lake Vanda waters which have a neutral to alkaline pH, however can simulate the slightly acidic waters beneath microbial mats in the lake's benthic environment (Webster *et al.*, 2003).

In the case of flooding, suprapermafrost fluids are unlikely to readily mix due to a very strong salinity gradient with overlying lake waters; additionally, these fluids lie 30-70cm under the soil (Webster *et al.*, 2003).

1.7 Rational for This Study

The last environmental assessment at the former Vanda Station site was competed nearly 20 years ago in 1997. Previous studies identified residual contamination with potential for environmental effects in Lake Vanda. Now, with Greywater Gully and many of the helicopter pads flooded, further study is required. This research aims to update our knowledge of the lasting environmental effects of Vanda Station. This research will address the level of contamination remaining, identify any continuing environmental effects, assess the effectiveness of remediation, and determine whether additional remediation will be required. This study addresses New Zealand's obligation to The Madrid Protocol to account for, and clean up past waste disposal sites.

1.7.1 Study Objectives

To test the hypothesis: ***Residual contamination at the Vanda Station site continues to affect water quality and cyanobacterial growth near this site,*** the following objectives are undertaken.

1. Determine residual contamination of contaminants at previously monitored, and new, sites; including trace metals, hydrocarbons and nutrients in soils, sediments and lake waters.
2. Assess the apparent response of benthic cyanobacteria to contaminants in flooded soils, and compare to predictions previously made (Hawes *et al.*, 1999).
3. Determine the release of contaminants from sediments and suprapermafrost fluids to Lake Vanda waters.
4. Assess and evaluate the effectiveness of the remediation efforts during decommissioning in 1993/94, and determine whether any additional remediation would be necessary at the former Vanda Station site.
5. Predict any ongoing effects of contamination on the main waterbody of Lake Vanda.

Chapter 2 - Methods

Water, sediment and soil samples were collected from the site of the former Vanda Station between the 7th and 11th of December 2014. Lake water, sediments and pore waters were collected from flooded sites and analysed for previously identified contaminants: trace metals, organic carbon, volatile organic carbon, petroleum hydrocarbons and nutrients (Webster *et al.*, 2003). Soils were collected from dry sites and analysed for trace metals, petroleum hydrocarbons, and underwent simulated leach tests. Additionally, the general chemical nature of water samples was determined. The pH, temperature, conductivity and dissolved oxygen were determined for all water samples, and general site descriptions recorded for all sites sampled.

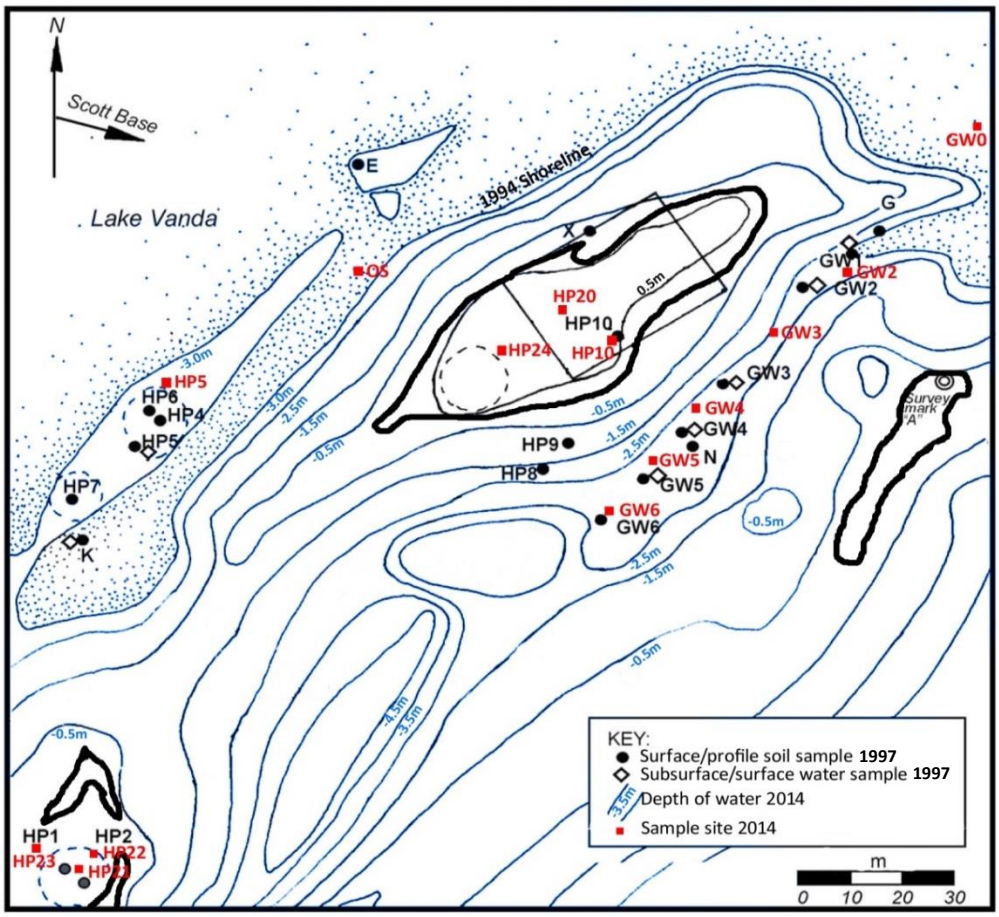


Figure 8 - Comparison of sampling locations at the former station and Greywater Gully in this study (red) and from Webster *et al* (2003) (black). Modified from Webster *et al* (2003), depth determined maps drawn prior to flooding. Thick black lines indicate present (Dec-2014) shoreline.

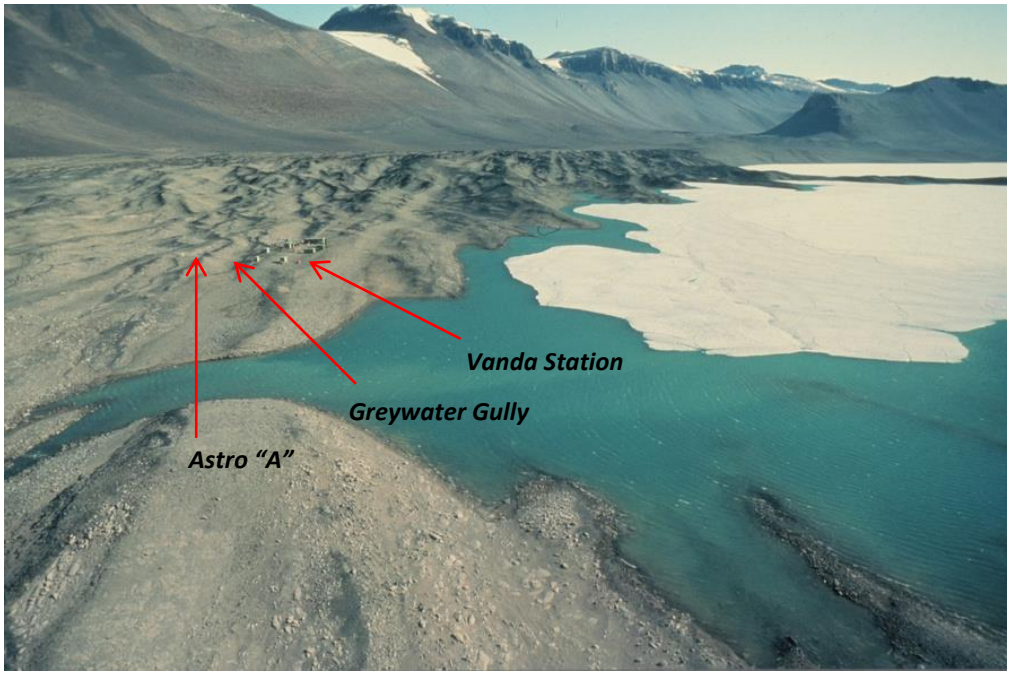


Figure 9 - Lake Vanda, Vanda Station and environs looking South West, circa 1980. Photo Kim Westerskov. (Antarctica NZ, 2015)

Figure 10 - Ariel view of the location of the former Vanda Station (larger island) looking west along the lake. Sampling locations are shown approximately for perspective only. Arrow indicates North (Photo taken 6/12/2015 by author).

2.1 Site Locations

2.1.1 Flooded Sites

Flooded site sampling locations (Figure 11) were chosen to align with sites of known soil contamination from prior studies (Figure 8) (Sheppard *et al.*, 1994; Webster *et al.*, 2003). Sampling locations were centred along the now flooded Greywater Gully (GW 0-6) and the main helicopter pads (HP 21-23), with additional contaminant sampling sites (HP5) and control sites (CG, VBG, OS) (Figure 10, Figure 11). GPS locations, bathometry and sampling depths are presented in Table 2.

Greywater Gully sampling locations were aligned along the deepest point in the now flooded gully, the exact locations of previously monitored GW sites are unknown as sampling predated widespread GPS use (Figure 8). Field work for Webster *et al* (2003) was undertaken in 1997, during which the lake level was at approximately 91.5m. The lake level at the time of the current sampling was 94.3m (McMLTER, 2015). This increase in lake level has flooded all Greywater Gully sites of the original sampling to a depth of 2.5-3m. All Greywater Gully sites were located through triangulation from known features shown on hand drawn maps from Webster *et al* (2003). Additional sites, "Off Station" (OS) and GW0, are deeper water sites to assess contaminant dispersion into the main body of Lake Vanda.

Sites HP21, HP22 and HP23 were located on the old main helicopter pad, which has experienced recent shallow flooding. These sites were easy to locate accurately from an orange painted marker rock on the north eastern edge of the old helicopter pad. This rock is the location of the GPS coordinate taken for HP21, HP22, and HP23. Actual site locations were measured from this point, all are in very close proximity.

The additional site HP5 was chosen to represent the old lower helicopter pad. The exact location of HP5 was difficult to determine, therefore a large potential error in its actual location exists.

Two control sites were chosen in flooded gullies with similar depth and surrounding bathometry to Greywater Gully; “Control Gully” (CG) and “Vanda Back Gully” (VBG) (Figure 10, Figure 11).

2.1.2 Dry sites

Sampling locations (Figure 11) for dry sites were chosen to represent visibly contaminated soils and sampling locations from Webster *et al* (2003). Fewer sampling locations were chosen as there was very little land of the former station and helicopter pads remaining above lake level. These sites, however, remain at risk of future inundation. Sites HP10 and HP20 were found by smelling the soil along the island for signs of hydrocarbon contamination. The site HP10 is a direct comparison to the same area sampled in Webster *et al* (2003). Site HP20 represents an obvious fuel spill, and site HP24 was a representative sample from the old helicopter pad. One control site was chosen, Control Gully soil (CGS), in “Control Gully” where the underlying and surrounding geology is similar to the former station site.

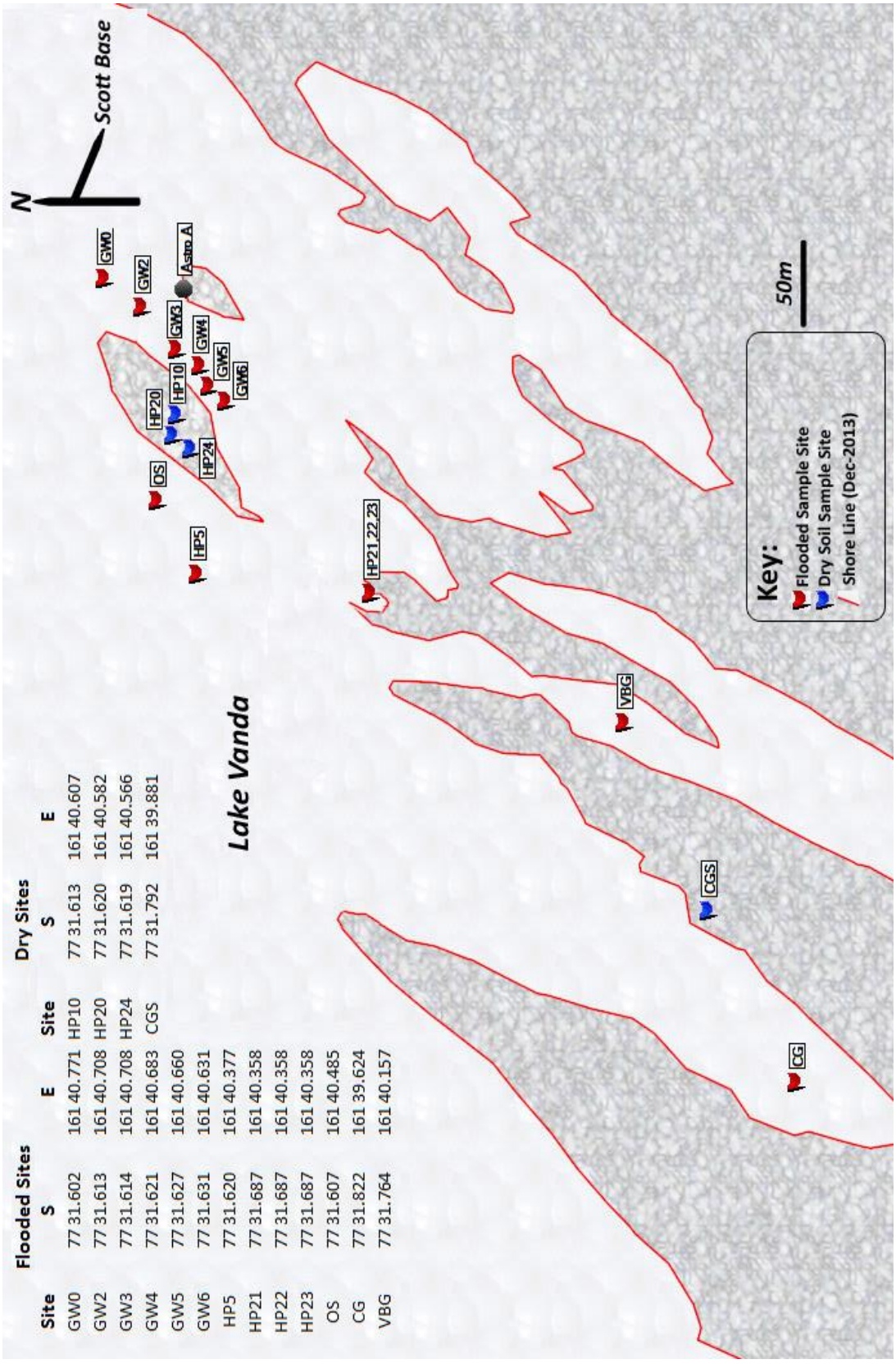


Figure 11 - Sampling area on Lake Vanda showing all flooded sampling locations (red) and soil sampling location (blue) and GPS coordinates. Map created by walking the shoreline with a GPS in 2013/2014 season (Ian Hawes), sampling points taken during field work for this study.

2.2 Sampling

2.2.1 Flooded Sites

All flooded sites, except HP21, HP22, and HP23 were covered with water and 2.0-2.3m of ice. The ice cap was drilled using a hand operated kovac auger taking care not to allow any ice waste to fall back in the hole. GPS coordinates were taken at each location, and the ice thickness and bathometry was determined using a modified weighted measuring tape. Bathometry measurements included both the total depth and piezometric level (depth to water level in ice hole) (Figure 12, Table 2, Table 3). Using a specifically designed water and pore water sampling pole (Figure 13), water samples were collected from immediately below ice cover (surface), midway, and at the benthic boundary layer. The sampling pole comprised of a rigid aluminium pole with PVC tubing running to a sealed sampling chamber at the base, to allow discrete sampling at specific depths. Water samples were drawn through the piping using a hand operated suction pump.

Porewater samples were collected from 5-15cm below the sediment surface following all lake water sampling to avoid potential cross contamination. These samples were taken using the same mechanism as lake water samples.

At each sampling location, following all water sampling, the sampling holes were expanded using a Jiffy Drill to allow for access of larger sampling equipment. Sediment samples were successfully collected from 2 sites (VBG, GW5) using an AMS 'Sludge and Sediment Corer™'. Sediment collection was unsuccessful at all other sites as the sediment was too rock-strewn to sample.

For the recently flooded sites, HP21, 22, 23, sampling was easier as the sites lay under only 0.1-0.15m of water plus 0.1m ice. For sampling, the ice cover was broken through using an ice axe, and field measurements were made. Water samples were collected from the surface, and porewater samples from 0.1m below the sediment, and sediment samples were taken by hand.

Samples were prepared by different means depending on the specific parameters to be analysed (Table 1).

Additionally, a video camera was lowered into the bore holes from GW0, GW4, GW5 and VBG to document the growth of cyanobacterial mats and to determine was there were any visually obvious signs of contamination under the surface.

Table 1 - Sample collection and preservation depending on type of analysis.

Sample type	Sites	Volume	Preservation
Volatile Organic Compounds (VOC's)	GW0-6, HP5, VBG, CG pore, basal waters. HP21 water	40ml	Ascorbic acid - glass jar
Total Organic Carbon (TOC)	GW0-6, VBG, CG basal waters	125ml	Unpreserved glass jar
Trace elements	All water, porewater samples	2 x 50ml	1 - filtered at 0.45µm, 1 - unfiltered. Plastic centrifuge tubes
Nutrients	All water, porewater samples	50ml	Filtered 0.45µm, plastic, frozen.
Major ions	All water, porewater samples	50ml	Unpreserved plastic tube
Hydrogen sulphide	All porewater samples	15ml	Zinc acetate preserved, plastic tube
Sediment core	VBG, HP21, HP22, GW5	250ml	Frozen, plastic sediment jar

Table 2 - Flooded sampling sites located within Greywater Gully. Included are the sample depths below ice surface, depth of porewater and sediments below lake bed, and thickness of ice.

Site	Sample Name	Depth	Thickness	Date	Sample Type
		m	m		
GWO	Ice	-	2.24		Ice
	Surface	2.24		7/12/2014	Lake Water
	Mid	2.92			Lake Water
	Bottom	3.6			Lake Water
	Porewater	0.1		8/12/2014	Porewater
GW2	Ice	-	2.06		Ice
	Surface	2.06		7/12/2014	Lake Water
	Mid	2.49			Lake Water
	Bottom	2.92			Lake Water
	Porewater	0.1		8/12/2014	Porewater
GW3	Ice	-	1.93		Ice
	Surface	1.93		7/12/2014	Lake Water
	Mid	2.39			Lake Water
	Bottom	2.85			Lake Water
	Porewater	0.15		8/12/2014	Porewater
GW4	Ice	-	2.08		Ice
	Surface	2.08			Lake Water
	Mid	2.79		7/12/2014	Lake Water
	Bottom	3.3			Lake Water
	Base	3.5			Lake Water
	Porewater	0.2		8/12/2014	Porewater
GW5	Ice	-	2.03		Ice
	Surface	2.03		7/12/2014	Lake Water
	Mid	2.67			Lake Water
	Bottom	3.31			Lake Water
	Porewater	0.15		8/12/2014	Porewater
GW6	Ice	-	1.8		Ice
	Surface	1.8		7/12/2014	Lake Water
	Mid	2.2			Lake Water
	Bottom	2.61			Lake Water
	Porewater	0.1		8/12/2014	Porewater

Table 3 - All other flooded sampling sites located outside of Greywater Gully. Included are the sample depths below ice surface, depth of porewater and sediments below lake bed, and thickness of ice.

Site	Sample Name	Depth	Thickness	Date	Sample Type
		m	**m**		
HP5	**Ice**	-	2.25	11/12/2014	Ice
	Surface	2.25			Lake Water
	Mid	2.57			Lake Water
	Bottom	2.9			Lake Water
	Porewater	0.1			Porewater
Control Gully (CG)	**Ice**	-	2.14	8/12/2014	Ice
	Surface	2.14			Lake Water
	Mid	2.75			Lake Water
	Bottom	3.77			Lake Water
	Porewater	0.1			Porewater
Vanda Back Gully (VBG)	**Ice**	-	2.18	8/12/2014	Ice
	Surface	2.18			Lake Water
	Mid	2.92			Lake Water
	Bottom	3.66			Lake Water
	Porewater	0.1			Porewater
Off Station (OS)	**Ice**	-	2.27	11/12/2014	Ice
	Mid	2.77			Lake Water
HP 21	**Surface**	0		9/12/2014	Lake Water
	Porewater	0.1			Porewater
HP 22	**Surface**	0		9/12/2014	Lake Water
	Porewater	0.1			Porewater
HP 23	**Surface**	0		9/12/2014	Lake Water

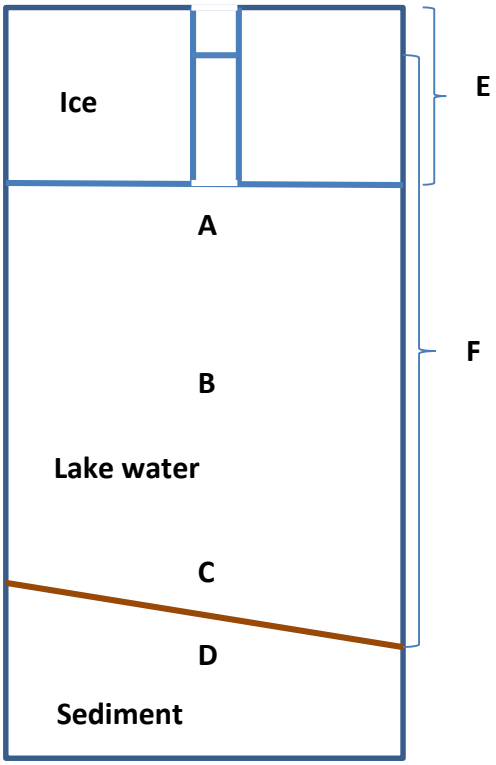


Figure 12 - Generalised profile of GW, HP5, CG and VBG sampling sites where A-C are water sampling depths, D - pore water and sediment sampling location, E - thickness of ice, F - depth of water (piezometric level).

Figure 13 - Sample collection and field measurements. Samples were drawn through water sampler via suction pump and sub sampled.

2.2.2 Dry Sites

Sampling of exposed soils was conducted on the 8th and 9th of December 2014 (Table 4). Soils at CGS and HP24 were collected as grab samples of surface soils, and at HP10/20 consisted of samples taken at varying depths throughout the soil profile (Table 4). All samples were collected using a clean plastic hand trowel and were sieved in the field at <2mm, to ensure a high proportion of the fine fraction for later analysis. Samples collected at each site were prepared and frozen for transport back to New Zealand. Three samples were taken from each site and depth; these were collected into;

- 150ml tin container, unpreserved for TPH,
- 250ml plastic container, unpreserved, provided by Hill Laboratories for trace elements,
- 300ml plastic container, unpreserved for leach tests.

Table 4 - Soils from dry sample sites, including depth of sample, location and date of sampling.

Site	Sample Depth	GPS		Date
		S	**E**	
HP10	0cm (Surface)	77' 31.613	161' 40.607	8/12/2014
	15cm			
	30cm			
	45cm			
HP20	0cm (Surface)	77' 31.620	161' 40.582	8/12/2014
	15cm			
	25cm			
HP24	0cm (Surface)	77' 31.619	161' 40.566	9/12/2014
CGS	0cm (Surface)	77' 31.792	161' 39.881	8/12/2014

2.3 Sample Analysis

Water and pore water samples were analysed immediately in the field for pH, temperature, conductivity and dissolved oxygen (DO) using a HACH™ HQ40d portable multi parameter field meter. The water column at sites GW2, GW3 GW4, GW5 and VBG was also analysed for pH and conductivity using a Conductivity, Depth and Temperature scanner (CDT scanner). Samples taken for later analysis were stored at Vanda Huts for the duration of field work. The samples were then transferred to Scott Base and either refrigerated or frozen prior to transport to New Zealand. All samples to be analysed for trace metals, TOC/VOC and major ions were air transported to New Zealand for storage in a refrigerated Ministry of Primary Industries (MPI) physical containment (level 1) (PC1) facility at the National Institute for Water and Atmospheric Research (NIWA) in Christchurch. Samples to be analysed for nutrients, and soil and sediment samples were frozen at Scott Base and transported to Christchurch via ship. Samples were sorted at NIWA in Christchurch, arranged for MPI transfer, and then distributed between a PC1 facility at Lincoln University, PC2 facility at University of Canterbury, or Hill Laboratories for analysis.

2.3.1 Trace Elements and Major Cations

Two water samples for metal determination were collected from every sampling location in 50ml centrifuge tubes. One sample was filtered at 0.45µm at the Vanda Huts for determination of dissolved metals, and one sample was left unfiltered for determination of total metals. Analysis blanks of milliQ water were added to the sample run, these were treated exactly as field samples.

All samples were acidified to pH <2 by the addition of 75µl ultra-pure nitric acid (HNO_3), then left for 3 weeks to allow for the dissolution of any metals bound to residual solids or the plastic container walls. All samples were subsampled, filtered at 0.22µm using Millex-GS™ 0.22µm filter and Chirana™ Luer 20ml syringe and transferred to inductively coupled plasma mass spectrometry (ICP-MS) tubes. The samples were filtered to allow removal from the PC2 facility and taken to the ICP-MS. Samples

with conductivity above 5000mS/cm were diluted 1:3 with 2% HNO_3 prior to analysis as a high salt content can create interferences in analysis.

Sediments and soils were prepared for analysis by the digestion of samples in hot nitric acid following the method in Webster *et al* (2003). Samples were dried at ~45°C until no change in weight was recorded and were sieved (<150µm). Approximately 0.1g of sediment was weighed into a Teflon beaker and 10ml of concentrated HNO_3 added. The Teflon beakers were placed on a hot plate on the highest setting and evaporated to almost dry; the beaker was refilled with 45ml of 0.1N HNO_3. This solution was further heated until <5ml remained; the samples were removed and left to cool. Once cool, the samples were transferred to 15ml centrifuge tubes and made up to ~10ml with 0.1N HNO_3. Final samples were prepared for trace metal analysis by ICP-MS.

A second set of digests were prepared to account for a cadmium anomaly in the initial results; the anomaly was likely due to contaminants present in the laboratory. Digestion blanks were prepared exactly as sample digests without any sediment.

All waters and digested sediments/soils were analysed for trace elements and major cations using ICP-MS. Analysis was done on an Agilent 7500 Series ICP-MS with an octopole reaction system at the University of Canterbury by Rob Stainthorpe. An internal standard of Rh was added online.

Quality Control/Quality Assurance

Table 5 shows QA/Qc data for ICP-MS analysis. Acid (1N nitric) and milliQ water blanks were analysed; these were filtered and diluted for quality control purposes. Digestion blanks were also analysed and duplicate samples were analysed in both the water samples and the digests. A certified standard, IV SRM 1643, was also analysed to test the accuracy of detection (Table 5). For full results including QA/QC data see Appendix 2 (waters).

Table 5 - QC data showing ICP-MS recovery of IV SRM 1643 standard reference material. Included are detection limits, trace element recovery in acid blanks and digest blanks.

		Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	Ag
Water QC											
DL[1]	**µg/l**	1	1	0.1	0.1	0.1	1	0.1	0.1	0.1	0.1
SRM concentration	**µg/l**	20	98	27	62	23	79	60	7	20	1
SRM Analysis	**µg/l**	21	140	28.8	61.9	20	72	59.3	7.1	19.9	<DL
Difference	**%**	5.0	42.9	6.7	-0.2	-13.0	-8.9	-1.2	1.4	-0.5	-100
Acid blank UF	**µg/l**	<DL	<DL	<DL	<DL	<DL	4	<DL	<DL	<DL	<DL
Acid blank F	**µg/l**	<DL	<DL	<DL	<DL	<DL	8	<DL	<DL	<DL	<DL
Soil digests QC											
DL[1]	**µg/L**	0.1	0.1	0.1	0.1	10	1	0.1	0.1	1	0.1
SRM concentration	**µg/L**	20.0	98	27	62	23	79	60	7	20	1
SRM Analysis	**µg/L**	22.3	126	28.1	64.4	20	77	64	7	20.7	0.82
Difference	**%**	11.5	28.6	4.1	3.9	-13.0	-2.5	6.7	0.0	3.5	-18
Digest blank	**µg/l**	1.4	99	<DL	0.3	10	29	1.2	2.9	2.1	0.5

1 – Detection limit, F - filtered sample, UF - unfiltered sample.

2.3.2 Total Organic Carbon

Total organic carbon (TOC) samples were collected into pre-prepared unpreserved amber 125ml glass jars provided by Hill Laboratories. Samples were analysed by Hill Laboratories in Hamilton. Total carbon (TC) was determined by persulphate oxidation and infrared detection; total inorganic carbon (TIC) was determined after acidification and purging. TOC = TC - TIC as per the standard method APHA 5310C (modified) (APHA, 2007). The detection limit for this method was 0.5g/m^3 (0.5mg/L).

2.3.3 Volatile Organic Compounds

Volatile organic compounds (VOC's) samples were collected into pre-prepared, ascorbic acid preserved amber 40ml glass jars provided by Hill Laboratories. Samples were analysed by Hill

Laboratories in Christchurch. VOC's were determined by purge and trap, and analysis by gas chromatography - mass spectrometry (GC-MS) (USEPA method 524.2; USEPA 1992). 64 VOC compounds were analysed (Appendix 4), with detection limits between 0.05g/m^3 (0.05mg/L) and 0.0005g/m^3 (0.0005mg/L). All samples were spiked with two quality control compounds to test % recovery. Quality control results indicated an average recovery of; 4-Bromofluorobenzine at 98.32% and Toluene-d8 at 100.26%.

2.3.4 Hydrogen sulphide

Hydrogen sulphide was determined photometrically by the APHA 4500-S^{2-} D methylene blue method by author at Lincoln University Waterways laboratory (APHA, 2007). 10 drops of amine-sulphuric acid and 3 drops of ferric chloride solutions were added to 7.5ml of sample, this reacts with the H_2S to produce a blue colour. 16 drops of diammonium hydrogen phosphate was added and the solution made up to 10ml with distilled water. Photometric determination was done on a HACH DR3900 spectrophotometer. This solution was photometrically analysed at 664nm using a pre prepared standard curve ranging from 0.1 - 2.0mg/L. Additionally, one duplicate and one blank were analysed. The duplicate and blank were both below the detection limit of the test. The detection limit for this test was 0.05mg/L.

2.3.5 Major anions

Major anions were determined via High Pressure Ion Chromatography (HPIC) by Roger Cresswell at Lincoln University. Samples were analysed on a Dionex DX-2100 Ion Chromatograph with an IonPac AS9-SC analytical column and IonPac AG9-SC guard column. Representative samples from each flooded site were analysed for the major anions nitrate (NO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}). The samples were analysed following filtration at 0.22µm (to allow removal from a PCI facility for analysis).

Quality Control/Quality Assurance

A filter blank, two standard references, and two duplicate samples were also analysed (QA/QC data is shown in Table 6).

Table 6 - QC data for major anion data including blanks, duplicate variances and standard reference variances.

	Cl^-	NO_3^-	SO_4^{2-}
Detection Limit	0.005mg/L	0.03mg/L	0.05mg/L
Filter Blank	0.03mg/L	0.2mg/L	0.07mg/L
Duplicate 1	1.6%	7.2%	0.4%
Duplicate 2	0%	0.3%	1.5%
Reference 1	2.5%	0.3%	0.7%
Reference 2	1.9%	0.3%	3.1%

Bicarbonate

Dissolved Inorganic Carbon (DIC) was measured as free CO_2 following acidification and purging on an ADC - 225 - MK3 CO_2 analyser by author at Lincoln University Waterways laboratory. Bicarbonate (HCO_3^-) in samples will form CO_2 when acidified below pH 4.5; so the CO_2 concentration in the vial headspace (pre-filled with N_2) is proportional to HCO_3^-in sample. A standard curve was produced using analytical grade sodium bicarbonate $NaHCO_3$ encompassing the concentrations expected in samples. These points included 0.001molL^{-1}, 0.002molL^{-1}, 0.005molL$^-$1, and 0.01molL^{-1} HCO_3^-. A 50ml syringe was filled with N_2 gas and 5ml of sample and acidified to <4.5 pH with 0.2ml concentrated phosphoric acid and mixed for 5 minutes. The standards were analysed by passing a 1ml, 2ml and 5ml of N_2/CO_2 mixture from the syringe headspace through the analyser and reading off the corresponding value. Once the standard curves were drawn and verified, samples were analysed by passing through 1ml, 2ml and 5ml of gas through the analyser. Readings were converted into molL^{-1}

HCO_3^- and then mgL^{-1} HCO_3^-. Results for 1ml and 2ml samples were used as the 5ml results were outside the area where the standard curve had precision. See Appendix 1 for standard curve and raw results.

Quality Control

A blank and four standards were analysed alongside the samples (Table 7). Additionally, each sample was read twice, using a 1ml and 2ml gas sample and read against the two different standard curves. The averages of these were taken.

Table 7 - QC data for the analysis of HCO_3^-. Four standards and one blank were included in the sample run and were analysed after the 10th and 20th sample.

	1ml Sample	2ml Sample	Average
0.005molL^{-1}	0.0053	0.0047	0.005
0.002molL^{-1}	0.0015	0.0016	0.00155
Blank	0.0007	0.0005	0.0006
0.01molL^{-1}	0.009	-	0.009
0.001molL^{-1}	0.0011	0.0012	0.00115

2.3.6 Nutrients

Waters and porewaters were analysed for nitrate and nitrite-nitrogen (NO_x-N) and DRP by Emma MacKenzie at Lincoln University Waterways laboratory.

NO_x-N was analysed by colorimetrically following cadmium reduction of nitrate to nitrite, and diazotisation forming a coloured dye. The nitrite proportion was measured via the same method without the reduction step (Mackereth, Heron, Talling, & Association, 1978).

DRP was measured calorimetrically via the molybdenum blue method where orthophosphate react with ammonium molybdate and potassium antimonyl which is then reduced forming an intense blue colour. This method follows the standard method 4500-P E (APHA, 2007).

2.3.7 Total Petroleum Hydrocarbons and PAH's

Total Petroleum Hydrocarbons (TPH) was analysed all soil samples and on the four sediment samples recovered, VBG, GW5, HP21 and HP22. GW5, HP20 (15cm, 25cm) and CGS were also screened for PAH's. Samples were analysed by Hill Laboratories in Hamilton using the USEPA 8015B method for TPH, where the samples are analysed by Gas Chromatography - Flame Ionization Detector (GS-FID) following sonication in a dichloromethane (DCM) extract. Detection limits range from 8-100 mg/kg. No QA/QC data was provided by Hill Laboratories.

2.3.8 TCLP Leach Testing

Simulated soil leaching was undertaken using an acidic and neutral leachate. Experimental leaching was undertaken by the author on all soil samples from HP10, HP20, HP24, and CG using a modified version of the United States Environmental Protection Agency (USEPA) Toxicity Characteristic Leaching Procedure (TCLP) Method 1311 (USEPA, 1992). Soils were used as sampled (<2mm fraction), with leaching solutions of distilled water (20ml to 1g soil) and 1N acetic acid (25ml to 1g soil) used. Samples were weighed into 50ml centrifuge tubes with leaching solution added, mixed for 20±1 hours then centrifuged at 4000rpm for 13mins. The leach tests were carried out at room temperature (22^{o}C). Final leachates were acidified to pH<2 and prepared for trace metal analysis by ICP-MS. Analysis for trace elements was undertaken as per Section 2.3.1.

Acetic acid leachates from CG, HP20 15cm and HP20 25cm were also analysed for PAHs (Appendix 4 for full list), determined via a liquid/liquid extraction and GC-MS SIM. The detection limit for individual PAHs range from 0.0001-0.0005g/m^3. PAH analysis was done at Hill Laboratories.

Quality Control/Quality Assurance

Final results from the first TCLP test showed some erroneous figures as indicated by the % recovery of Rh (an internal standard used for calibration) which showed results around 200% for the acetic acid leachates. These results had to be recalculated, as the high rhodium recovery distorted the trace metal and cation concentrations measured. The acetic acid leachate blank results also contained high concentrations of trace metals. The test was carried out a second time using certified clean acetic acid. Rhodium recovery in the ICP-MS was still high (200%) in all of the samples as Rh ion is used as a catalyst during acetic acid formation (Jones, 2000); this was corrected for during analysis on the software in the ICP-MS. Final QA/QC data is presented in Table 8.

Table 8 - QA/QC data for trace element analysis on TCLP leachates.

		Cr	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	Mn
DL[1]	µg/L	0.1	0.1	0.1	0.1	0.1	1	0.1	0.1	1	0.1
SRM concentration	µg/L	20.0	98.0	27.0	62.0	23.0	79.0	60.0	7.0	20.0	39.0
SRM analysis	µg/L	18.5	111.7	24.0	55.0	17.8	68.5	54.1	6.8	18.8	37.8
Difference	%	-7.9	12.2	-12.3	-12.8	-29.2	-15.3	-10.9	-2.4	-6.3	-3.3
Blank Water	µg/L	0.1	3.4	<DL	<DL	<DL	<DL	<DL	<DL	1	0.3
Blank Acetic	µg/L	0.5	10.1	<DL	2.4	<DL	22	0.2	0.7	1	0.2

1 – Detection limit

2.5 Errors and Omissions

Errors in analysis can come from a number of different sources; sampling, transport and handling contamination; instrument error; and human error in sampling, preparation and analysis of samples. Care was taken to ensure minimal cross contamination of samples, mixing of samples, loss of samples, and accuracy in analysis. An outline of quality control was included in each of the method descriptions.

2.5.1 Difficulties in working in Antarctica

A common source of error in working with Antarctic sample contamination. Unforeseen problems, mis-sampling and misplaced gear for sampling cannot be rectified, due to the logistics of getting personal and equipment into the field. Consequently, any damaged or lost samples in transition or in the laboratories cannot be resampled. Only one sample was lost in transit due to tube splitting and sample spilling into the secondary container; the major ions sample for control gully porewater.

Chapter 3 - Results

The results for this study are presented in three sections: Section 3.1 outlines the results for all water samples and porewater samples from Greywater Gully, the helicopter pads and control sites. Cyanobacterial observations in flooded sites are outlined in Section 3.2. Contaminant results for non-flooded soils and flooded sediments are presented in Section 3.3.

The Australia New Zealand Environmental and Conservation Council (ANZECC) guidelines were used to assess the significance of contaminants in water and sediment (ANZECC, 2000). These guidelines were developed for temperate systems rather than Antarctic freshwater or marine systems. The trigger values for the protection of 95% and 99% of species however, are a useful guideline as to what could be acceptable in this ecosystem in the absence of more appropriate guidelines.

3.1 Lake Waters

Water sampling sites were grouped into three categories: Greywater Gully, helicopter pads and control sites. All results are presented and described together according to the analysis type.

3.1.1 Site Descriptions

Greywater Gully

Greywater gully is orientated NE-SW for approximately 50m, from 77' 31.613 S, 161' 40.708 E to 77' 31.631 S, 161' 40.631 E. The bathymetry along the centre of Greywater Gully was determined during sampling (Table 2). The method lacks fine resolution between points GW0 and GW2, as seen in Figure 14 and Figure 15. Figure 15 indicates a slight depression in the gully between GW5 and GW3 before a rise towards GW3 and GW2. The bottom of Greywater Gully lies beneath between 3.5m (GW4) and 2.85m (GW3) of water, much of which was an ice cap of between 1.8m and 2.06m thick, at the time of sampling. The ice surface was clean and free of debris, and there were no irregular

colours or aromas from any water samples drawn up, except from GW4 and GW5. Porewater samples from GW4 and GW5 smelled of hydrocarbons and had a surface scum, upon the retrieval of sample.

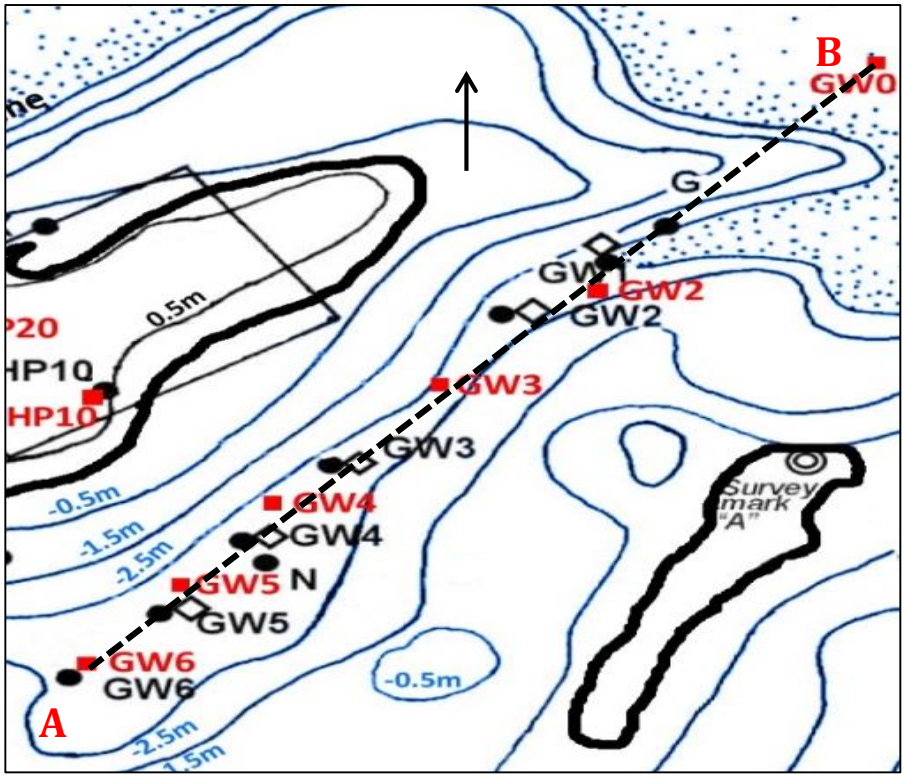


Figure 14 - Close up of Greywater Gully as taken from Figure 8. The black transect line relates to the profile in Figure 15.

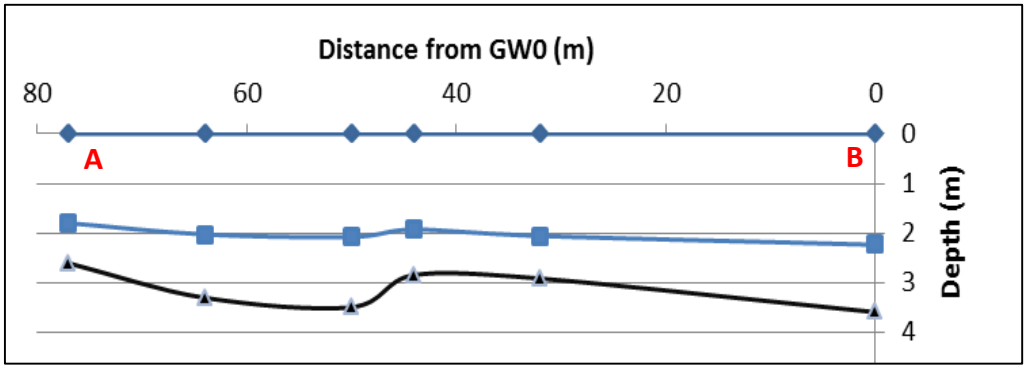


Figure 15 - Depth profile of Greywater Gully from A-B (Figure 14). Black line (triangles) represents the lake bed; the blue lines represent the top and base of the ice cap. Points from left to right are: GW6, GW5, GW4, GW3, GW2, GW0.

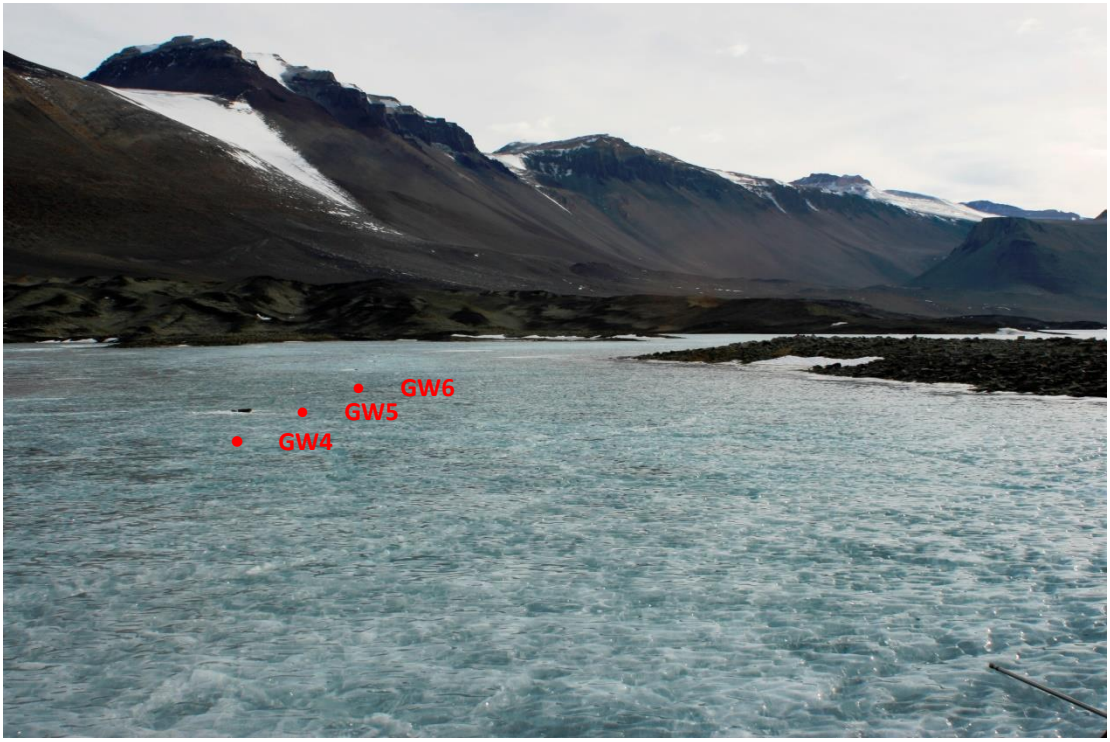


Figure 16 - Greywater Gully looking west from a site north of GW3 towards GW4, GW5 and GW6. The island on the right is the location of the former Vanda Station.

Helicopter Pads

The former main helicopter pads were located to the west of the former station (Figure 10, Figure 11); and were marked out using orange painted rocks. While these rocks now form the boundary for the new helicopter pad at the Vanda Huts, some painted rocks remain in position at the former pads (Figure 18). The helicopter pads have been recently inundated by Lake Vanda and lie at a depth of 15cm (Figure 17). There was no observable sign of contamination in the water around HP21, HP22, and HP23 except for the painted marker rocks and litter. Cyanobacterial mats were observed in the vicinity of the helicopter pads (Figure 30). The helicopter pad site HP5 lay further into Lake Vanda. The depth of water prohibited observation of any signs of contamination.

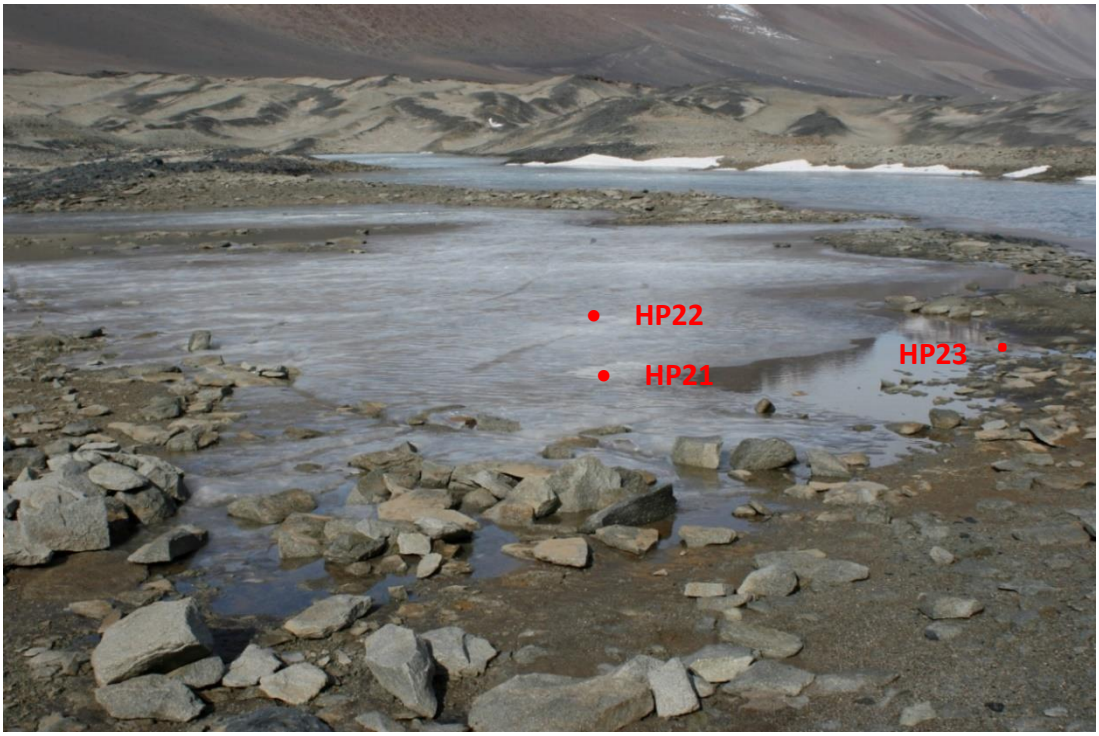


Figure 17 - Recent inundation of the former main helicopter pad and location of sampling points HP20, HP21 and HP23.

Figure 18 - Orange painted rock at the edge of Lake Vanda in the vicinity of HP21.

Control Sites

Three control sites were sampled. Site CG was located at the head of "Control Gully" with surrounding bathymetry similar to GW3, GW2 and GW0. This site is connected to the main waterbody of Lake Vanda. VBG was located partway up a gully cut off from the main waterbody by ice. This ice barrier prevents mixing with lake water and creates a zone of cryoconcentration of dissolved salts. This process is similar to processes undergone in GW4, GW5 and GW6, where the basal waters are likely to have undergone cryoconcentration throughout the winter. Site OS is a semi-control, only one water sample was taken mid-way down the water column.

3.1.2 Major Ion chemistry of Lake Water

Major ions were measured in all water samples collected in Greywater Gully, the helicopter pads and control sites (see Appendix 1 for the full dataset). Only 21 representative water samples were analysed for Cl^-, SO_4^{2-} and HCO_3^-, these results were plotted against the sample's conductivity with a linear regression analysis. The major anion concentrations for the remaining 18 samples was calculated from this regression based on their conductivity.

The anionic compositions of the waters of Lake Vanda are dominated by Cl^- with lesser concentrations of HCO_3^- and SO_4^{2-} (Table 9). Cl^- dominance increases with depth (Figure 20), with the molar ratio HCO_3^-:Cl^- decreasing with depth, from HCO_3:Cl^- of 0.61:1 at the surface to 0.18:1 in the basal water (Figure 20, Figure 19).

The cation chemistry in the waters of Lake Vanda is dominated by Ca^{2+} and Na^+ with lower concentrations of Mg^{2+} and K^+ (Table 9). The relative molar concentrations of Na^+, Ca^{2+} and Mg^{2+} are expressed in Figure 19. All water samples analysed contained very similar cation ratios of Na^+:Ca^{2+}:Mg^{2+} 47:37:16, this does not change with depth. The total concentration of all major ions, however, increases with depth.

Table 9 - Major ion chemistry in lake and porewaters in Lake Vanda. Displayed are the average concentrations (mg/L) for all sites excluding VBG at each depth.

	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}
Surface (n=20)	11.7	4.4	3.4	14.1	54.9	48.1	3.3
Mid (n=18)	53.8	16.3	19.7	79.5	78.3	243.3	18.0
Base (n=18)	62.1	18.7	24.9	91.8	87.1	308.8	22.7
Porewater (n=9)	77.7	20.3	26.5	99.7	92.7	343.9	28.4

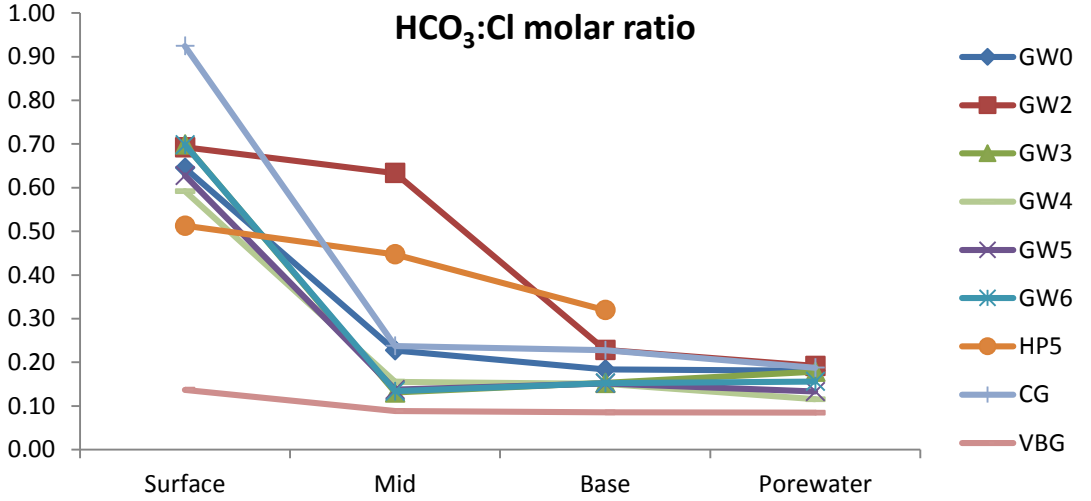


Figure 20 - Anionic molar concentration ratio between HCO_3^- and Cl^- showing the increasing dominance of Cl^- with depth in the water column.

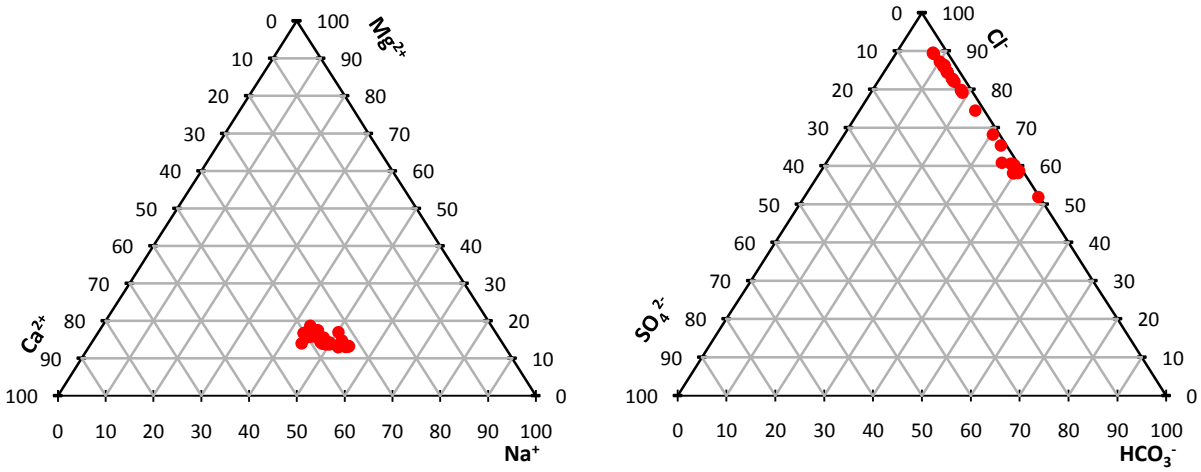


Figure 19 - Ternary diagram showing major cation (left) and anion (right) chemistry in all water samples from Lake Vanda based on % of total molar concentrations.

3.1.3 General Water Quality Parameters

The pH, conductivity, DO and temperature were measured on water samples at all sites during sampling. Following this, the pH and conductivity profile were measured for water columns at sites GW2, GW3, GW4, and GW5 using a CDT scanner (Figure 24).

The pH in Lake Vanda as measured in all water profile samples ranged from an average of 8.86 at the surface, 8.35 in mid waters, and 8.22 in the basal waters (Figure 21, Figure 22, Figure 23). The pH in the porewaters was significantly lower at 7.17[b]; many of which were of neutral pH rather than the slightly alkaline pH measured in lake waters (Table 10). The recently flooded helicopter pads had a pH averaging 7.9 (Table 11).

The conductivity in Greywater Gully ranged from an average of 212µS cm^{-1} at the surface, 1016µS cm^{-1} midway, and 1201µS cm^{-1} in the basal waters (Figure 23, Figure 24). On the helicopter pads, the conductivity averaged 508 at HP21/22 and 170 at HP23 (Table 11). The conductivity in control samples ranged from 179µS/cm to 964µS/cm in CG and 2016µS/cm to 5150µS/cm in VBG (Figure 22). The conductivity in the porewaters was not significantly different to the basal water[c].

The temperature at all sites increased with depth from close to 0°C at the bottom of the ice layer to between 2.5-4.9°C in the basal waters.

Dissolved oxygen increased with depth at all sites sampled except for GW6. In Greywater Gully the DO ranged from an average of 10.1mg/L at the surface, 11.4mg/L midway and 14.7mg/L in the basal waters (Figure 23). Twelve discrete samples had a DO higher than the detection limit of 20mg/L for the HACH GQ40d probe.

[b] 1 tailed t-test, unpaired variances between pH of lake water (mean 8.47, n 29) and porewaters (mean 7.18, n 8) ($p<0.005$).

[c] 1 tailed t-test, unpaired variances between conductivity of basal waters (mean 1628, n 9) and porewaters (mean 1885, n 8) ($p=0.37$).

Table 10 - pH, conductivity, and DO in pore water samples taken from Greywater Gully sites. Samples depth is metres below lake bed.

Site	Depth	pH	Cond	DO
	m		µS/cm	mg/L
GW0	0.1	7.25	1000	10.99
GW2	0.1	7.28	920	11.19
GW3	0.15	7.52	1021	11.04
GW4	0.2	7.38	2260	10.77
GW5	0.15	6.93	1685	9.66
GW6	0.1	6.81	1264	11.1

Table 11 - pH, conductivity, temperature and DO results from HP sites.

Site	Sample	Depth	pH	Cond	Temp	DO
		m		µS/cm	°C	mg/L
HP 21	**Surface**	-	8.28	501	-	9.87
HP 22	**Surface**	-	7.99	516	-	9.8
HP 23	**Surface**	-	7.5	170	2.6	11.58

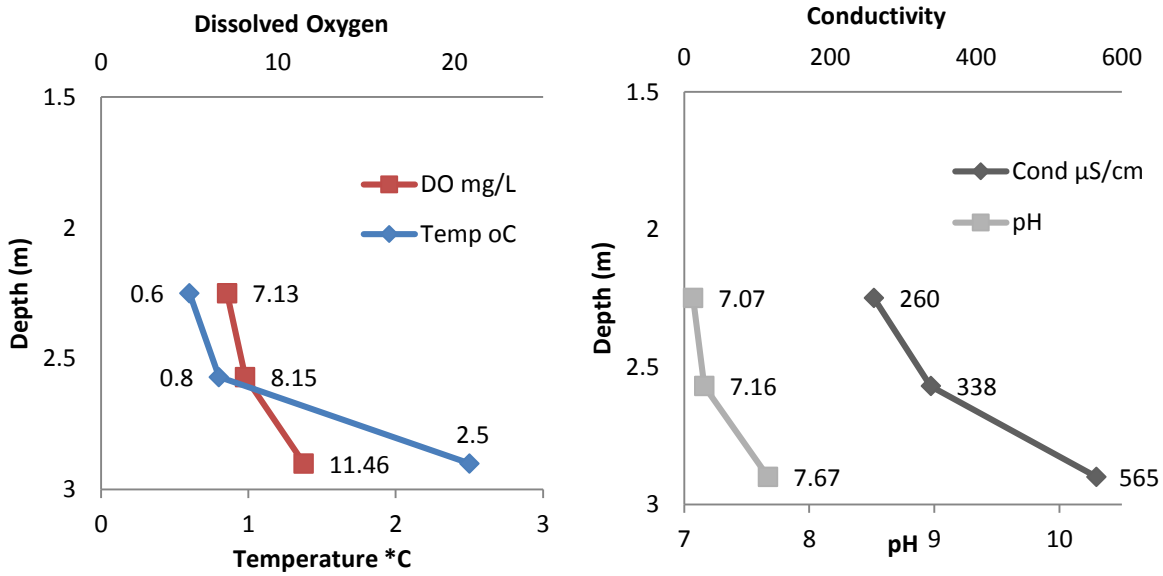


Figure 21 - Temperature, DO, conductivity and pH profile for HP5 as measured on water samples collected at different depths. The ice cap occupies the first 2.2m of the profile.

Table 12 - pH, conductivity, temperature and DO results the OS control site.

Site	Sample	Depth	pH	Cond	Temp	DO
		m		µS/cm	°C	mg/L
Off Station (OS)	**Mid**	2.77	7.58	965	2.4	15.18

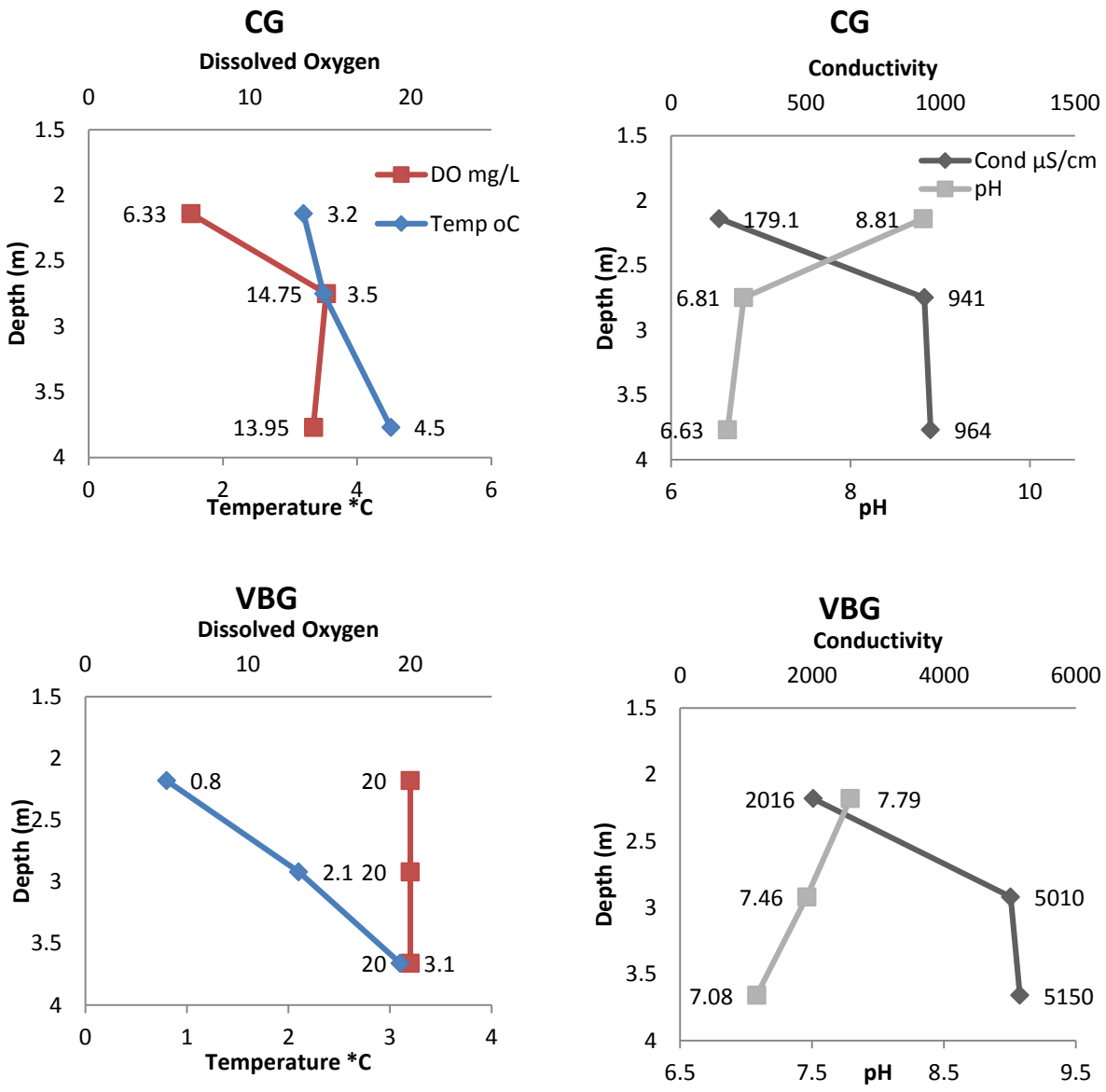


Figure 22 - Temperature, DO, conductivity and pH profiles for CG and VBG as measured on water samples collected at different depths. Ice cap occupies the first 2.1-2.2m of the each profile.

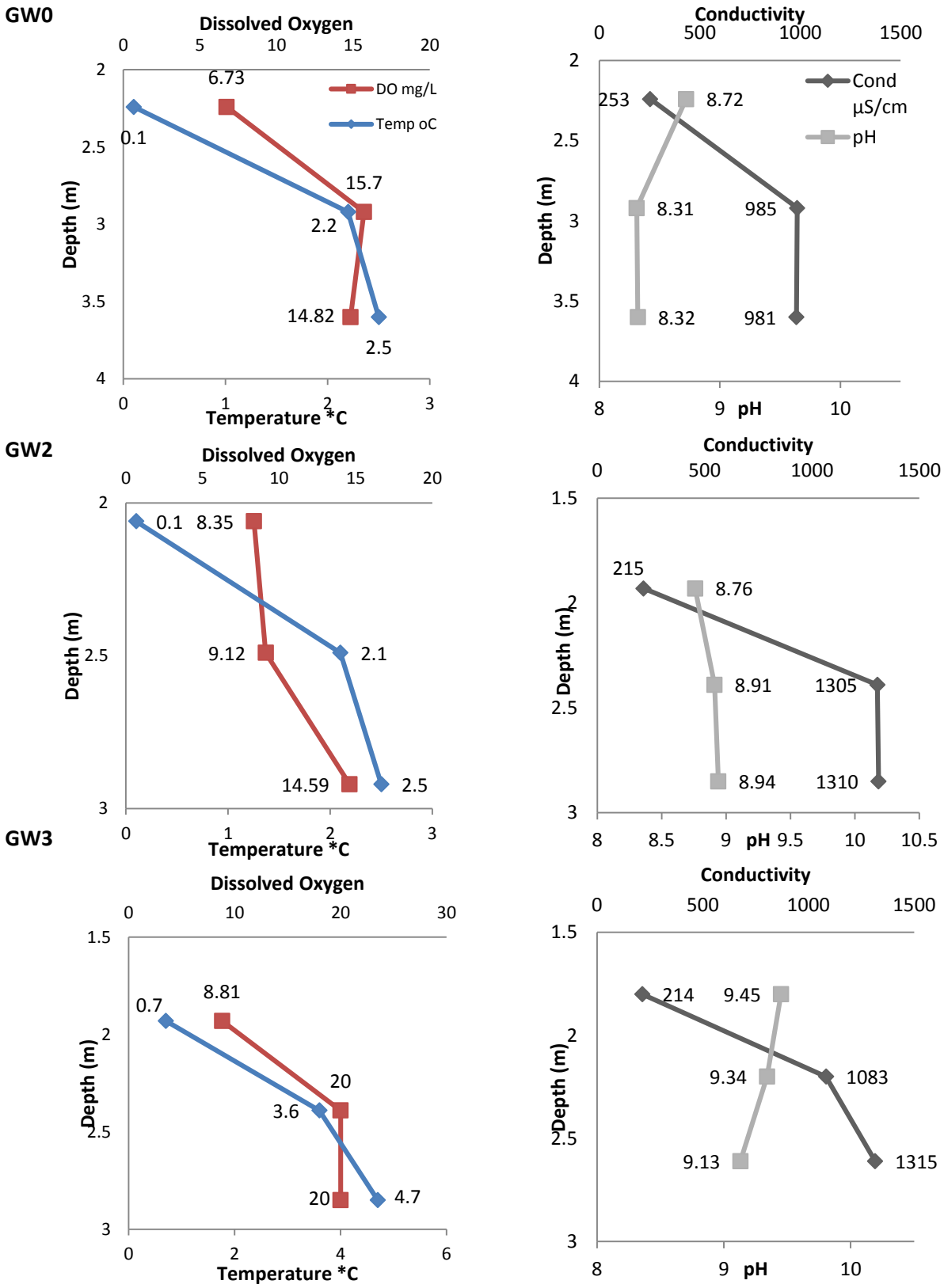


Figure 23 - Temperature, DO, pH and conductivity results for surface waters in Greywater Gully as taken on water samples collected at different depths. The ice cap occupies the first 1.5-2.0m of each profile.

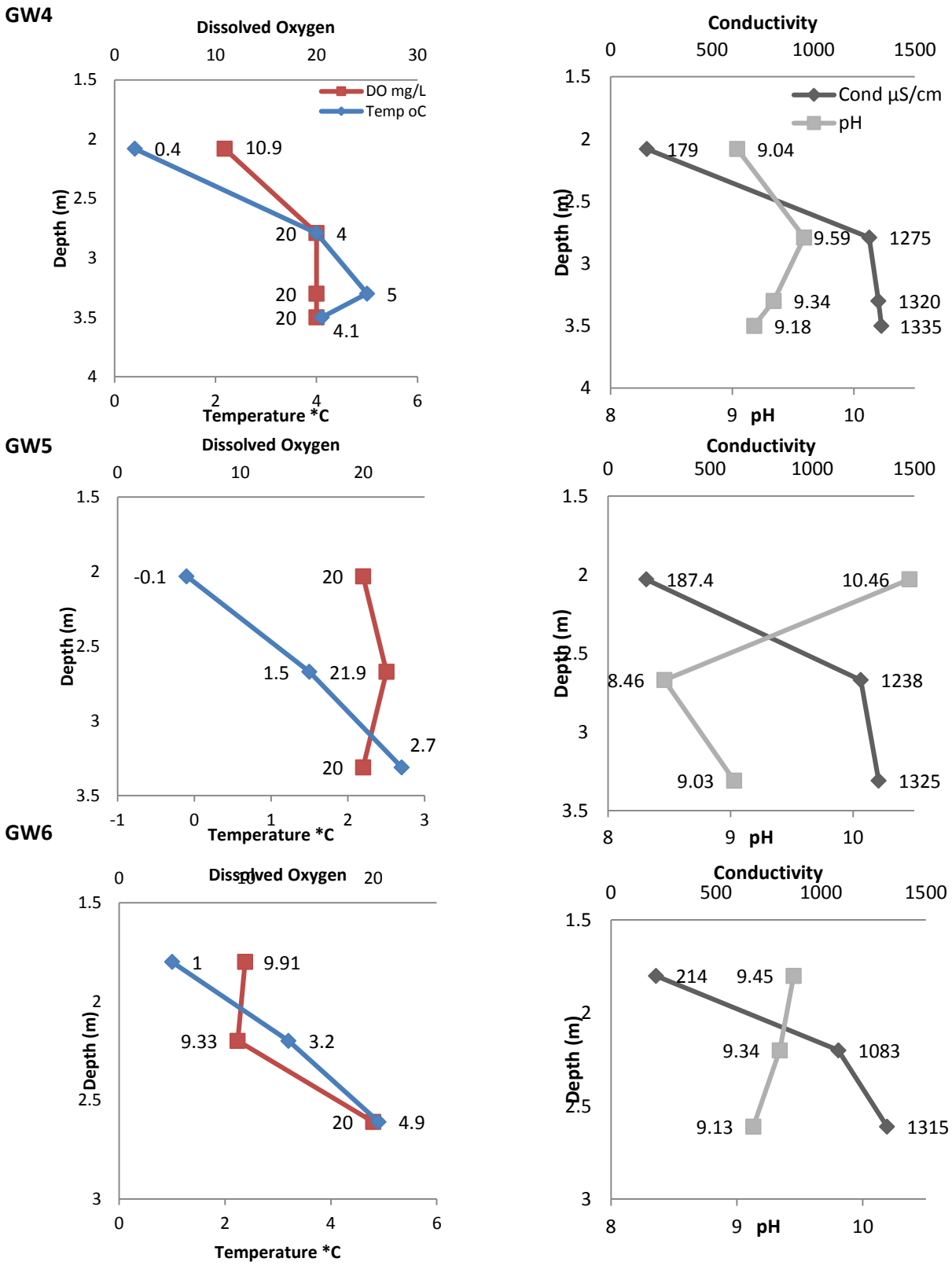


Figure 23b - Temperature, DO, pH and conductivity results for surface waters in Greywater Gully as taken on water samples collected at different depths. The ice cap occupies the first 1.5-2.0m of each profile.

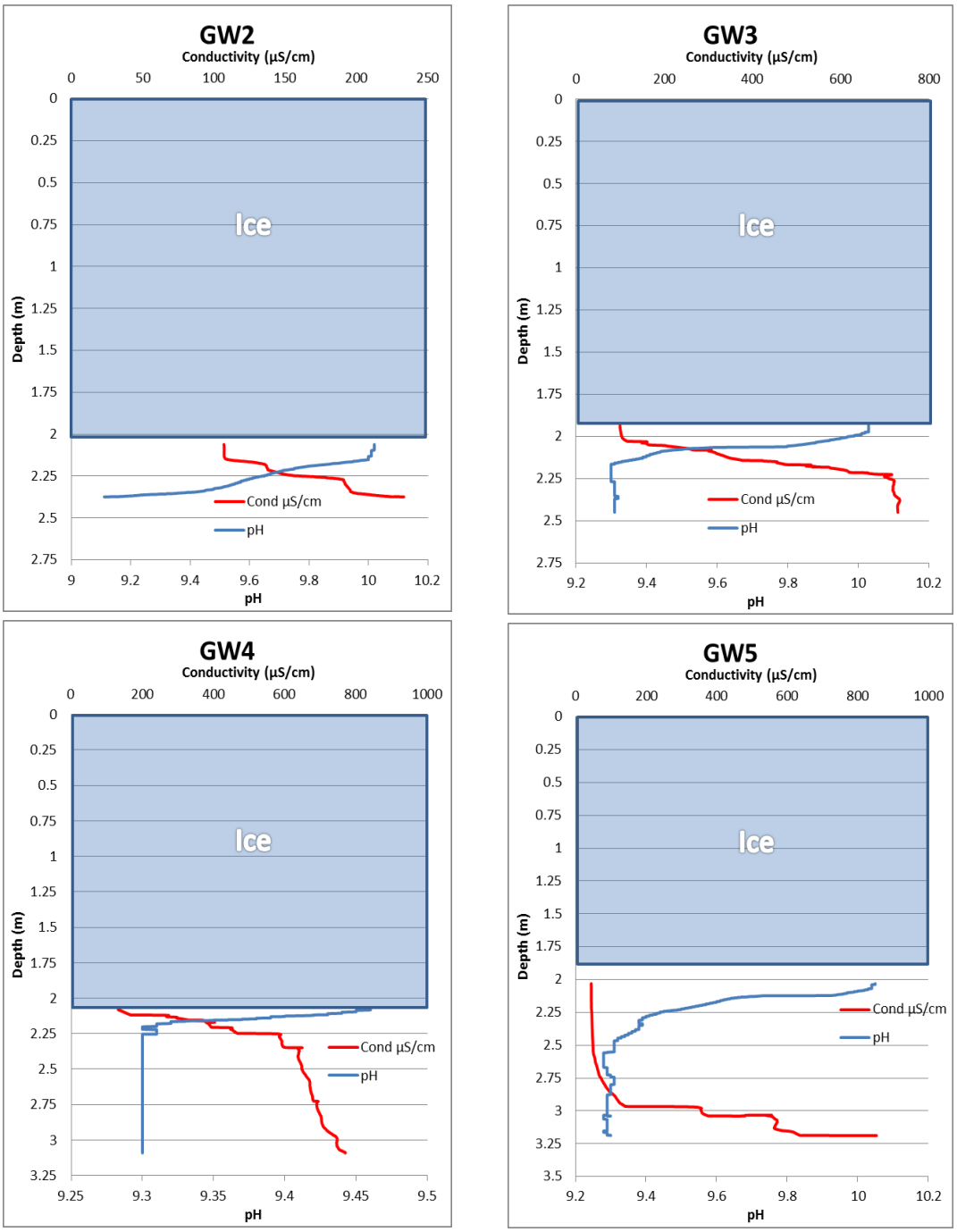


Figure 24 - Conductivity and pH profiles as measured using the CDT scanner. Note that measurements started at the base of the ice layer, not in the access hole drilled through the ice cap.

3.1.4 Trace Elements

Water and porewater samples were analysed for Pb, Zn, Cd, Ni, Co, Cu, Ag, Fe, Mn, As and Cr. See Appendix 2 for full dataset.

Table 13 - Maximum total concentrations (µg/L) of trace elements measured in each water profile (i.e. 3 depths and porewater sample). Included are the 95% and 99% ANZECC trigger values.

	Ag	As	Cd	Co	Cu	Cr	Fe	Mn	Ni	Pb	Zn
Detection Limit	0.1	0.1	1.0	0.1	0.1	1.0	1.0	1.0	0.1	0.1	1.0
ANZECC 95%	0.05	24	0.2	-	1.4	1.0	-	1900	11	3.4	8.0
ANZECC 99%	0.02	1.0	0.06	-	1.0	0.01	-	1200	8	1.0	2.4
Greywater Gully											
GW0	<0.1	0.2	<1.0	0.2	0.8	1.0	239	6.0	0.5	1.0	99
GW2	<0.1	0.2	<1.0	<0.1	1.1	<1.0	12	1.0	1.8	1.2	120
GW3	<0.1	0.2	<1.0	<0.1	0.8	1.0	8.0	<1.0	0.6	1.3	118
GW4	<0.1	0.3	<1.0	0.1	1.1	1.0	84	35	5.4	1.5	287
GW5	<0.1	1.2	<1.0	<0.1	1.0	<1.0	58	1888	3.9	0.8	51
GW6	<0.1	0.4	<1.0	<0.1	1.3	<1.0	7.0	7.0	0.5	0.7	61
Helicopter Pads											
HP21	<0.1	0.7	0.1	0.2	2.1	<1.0	225	5.0	0.6	0.5	10
HP22	<0.1	0.3	<0.1	<0.1	2.1	<1.0	4.0	2.0	0.3	0.2	1.0
HP23	<0.1	<0.1	<0.1	<0.1	0.9	<1.0	23	<1.0	0.2	<0.1	3.0
HP5	<0.1	0.2	<0.1	<0.1	0.9	1.0	26	<1.0	0.4	0.2	272
Control Sites											
CG	<0.1	<0.1	<0.1	<0.1	0.4	<1.0	6	<1.0	0.4	0.9	311
VBG	<0.1	1.0	<0.1	0.2	1.5	4.0	30	36	1.7	0.9	135
OS	<0.1	<0.1	<0.1	<0.1	0.2	<1.0	10	<1.0	0.3	0.2	22

Silver was not detected in any water sample. Cd was only detected in one sample, HP21 porewater. There are no anomalous concentrations of Cd or Co in any sample; results are either below the

detection limit or comparable to control sites. Cr was detected in 11/72 samples, all samples below the surface water from the control VBG exceeded the ANZECC guidelines 95% trigger value of 1µg/L for Cr.

Copper was detected in 66/72 samples from water profiles ranging from 0.1-2.1 µg/L at concentrations averaging 0.6µg/L in Greywater Gully samples, 1.5µg/L in HP samples, and 0.6µg/L in control samples. The ANZECC 99% trigger value was exceeded in 12 samples, 4 from the HP sites, 2 from VBG, and the 95% trigger value was exceeded 4 times, 3 in the HP sites and once in VBG (Figure 26, Figure 27, Figure 28).

Zinc was detected in all samples from water profiles ranging from 1-311µg/L and there was no difference between control sites and GW/HP sites. There is an observed concentration gradient from high (shallow water) to low (deep water) concentration in most water profiles (Figure 26, Figure 27, Figure 28). Most of the detected Zn (79%) was in a dissolved and bioavailable form. Most sites had samples exceeding the ANZECC 95% trigger value (2.4µg/L) for Zn. Zinc was much lower in concentration in the recently flooded HP21-23 sites where the average concentration was 6.7µg/L.

Lead was detected in all water profiles (<0.1-1.5µg/L) and some shallow site samples (<0.1-0.5µg/L). Higher concentrations were detected in deeper samples and 53% of Pb measured in samples was dissolved. The ANZECC 99% trigger value for Pb (1.0µg/L) was exceeded by 8 samples in Greywater Gully; the 95% trigger value (3.4µg/L) was not exceeded by any sample (Figure 26, Figure 27, Figure 28).

Arsenic was detected in the basal and porewaters from most sites between 0.1-1.2µg/L. Three samples exceeded the ANZECC 99% trigger value (1.0µg/L), GW5 porewater, VBG porewater, and VBG basal (uf - Total). There was very little difference between dissolved and total As in samples. Nickel was detected in all samples at a similar concentration to control samples; only GW4 bottom

(total) and GW5 porewater were elevated at 5.4µg/L and 3.9µg/L. All samples fell below the ANZECC 99% trigger value of 8.0µg/L (Figure 26, Figure 27, Figure 28).

Manganese was detected in only 18/72 samples, usually only porewater and basal waters. One sample, (GW5) porewater exceeded the ANZECC 99% trigger value of 1200µg/L. Iron was detected in all samples with an average concentration of 16.1µg/L, three samples had substantially higher concentrations, see Figure 25.

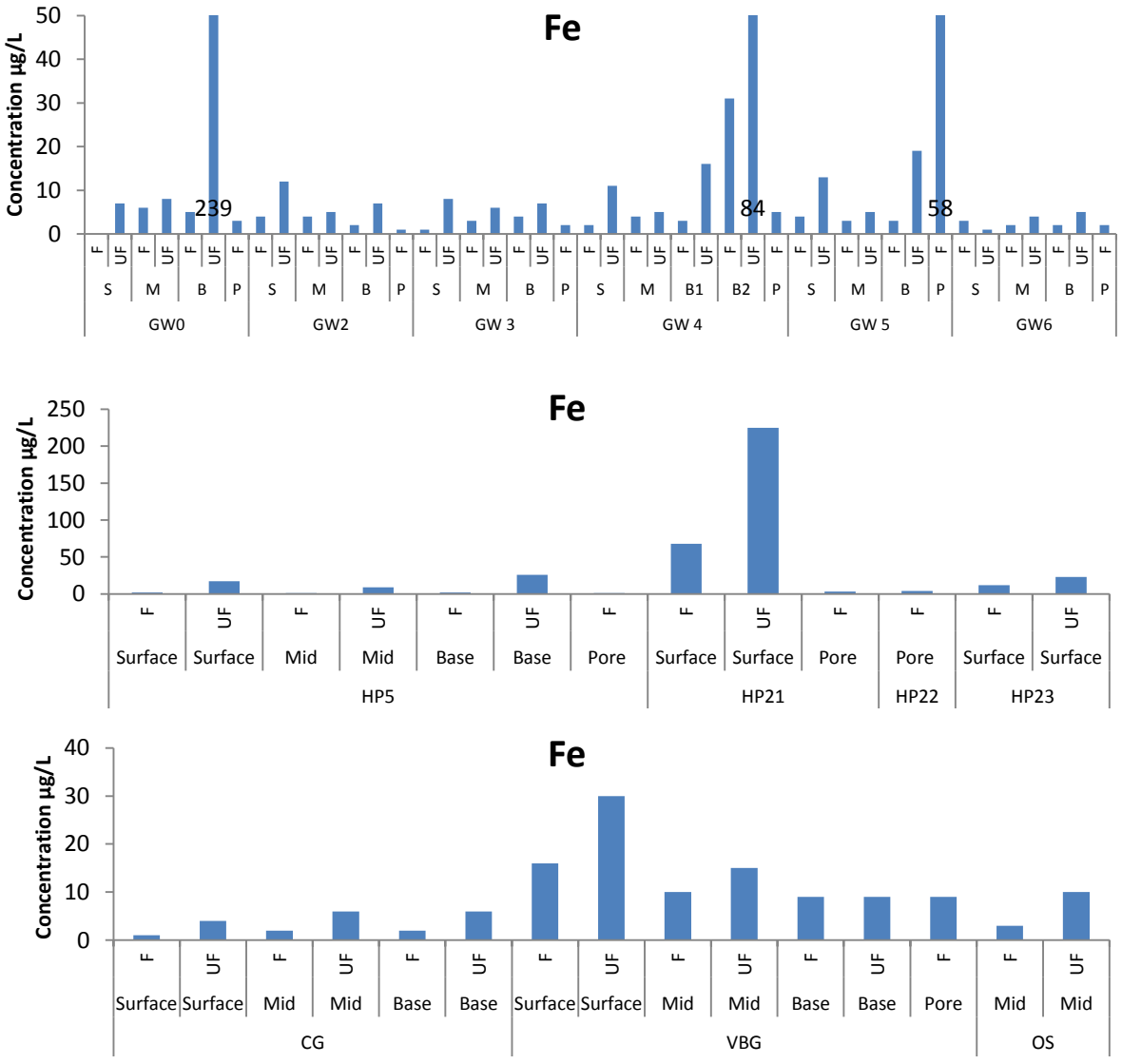


Figure 25 - Iron concentrations in Greywater Gully, HP and control sites showing dissolved (f) and total (uf) concentrations.

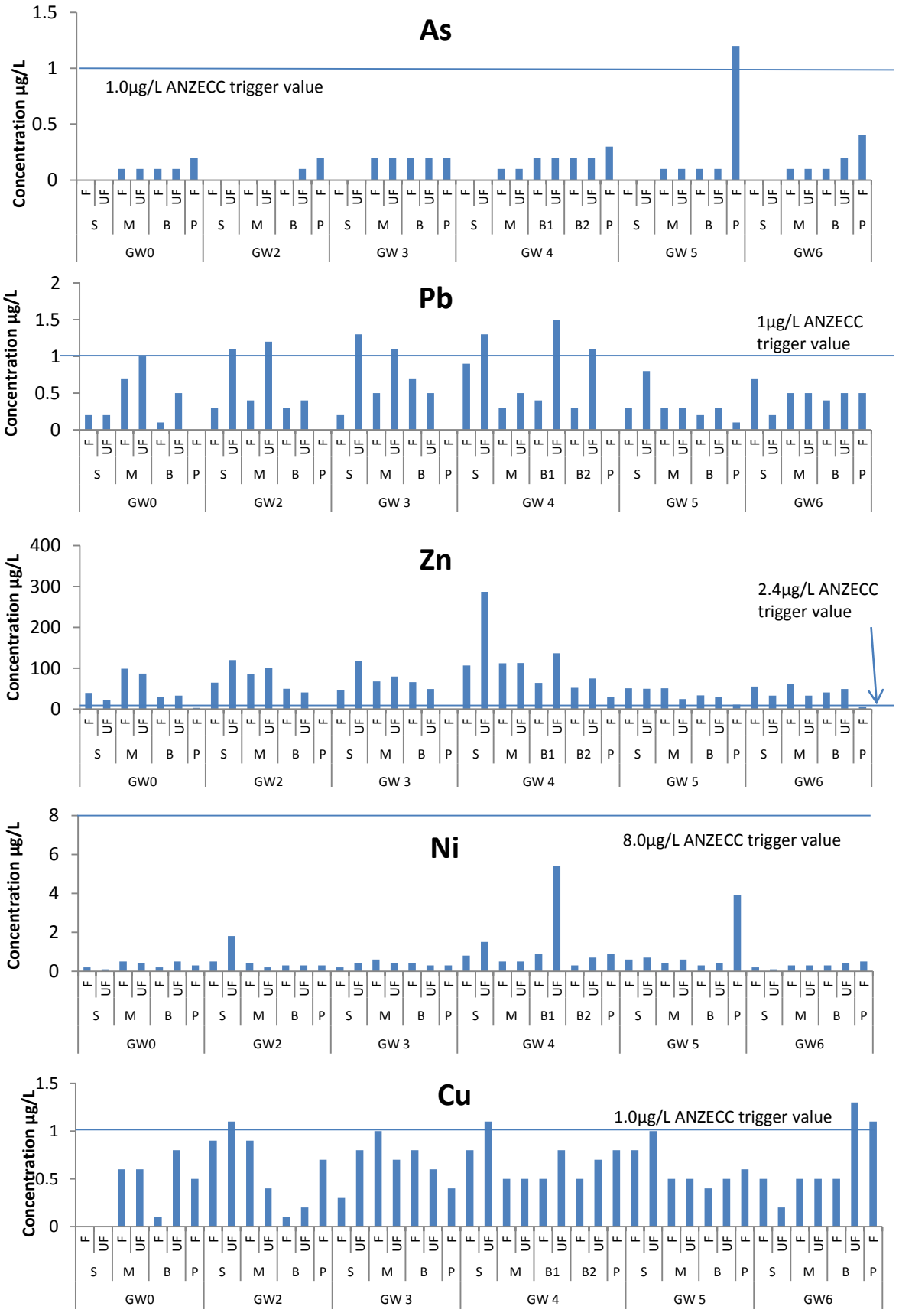


Figure 26 - Trace elements in Greywater Gully water and porewater samples showing dissolved (f) and total (uf) concentrations and the ANZECC 99%trigger value.

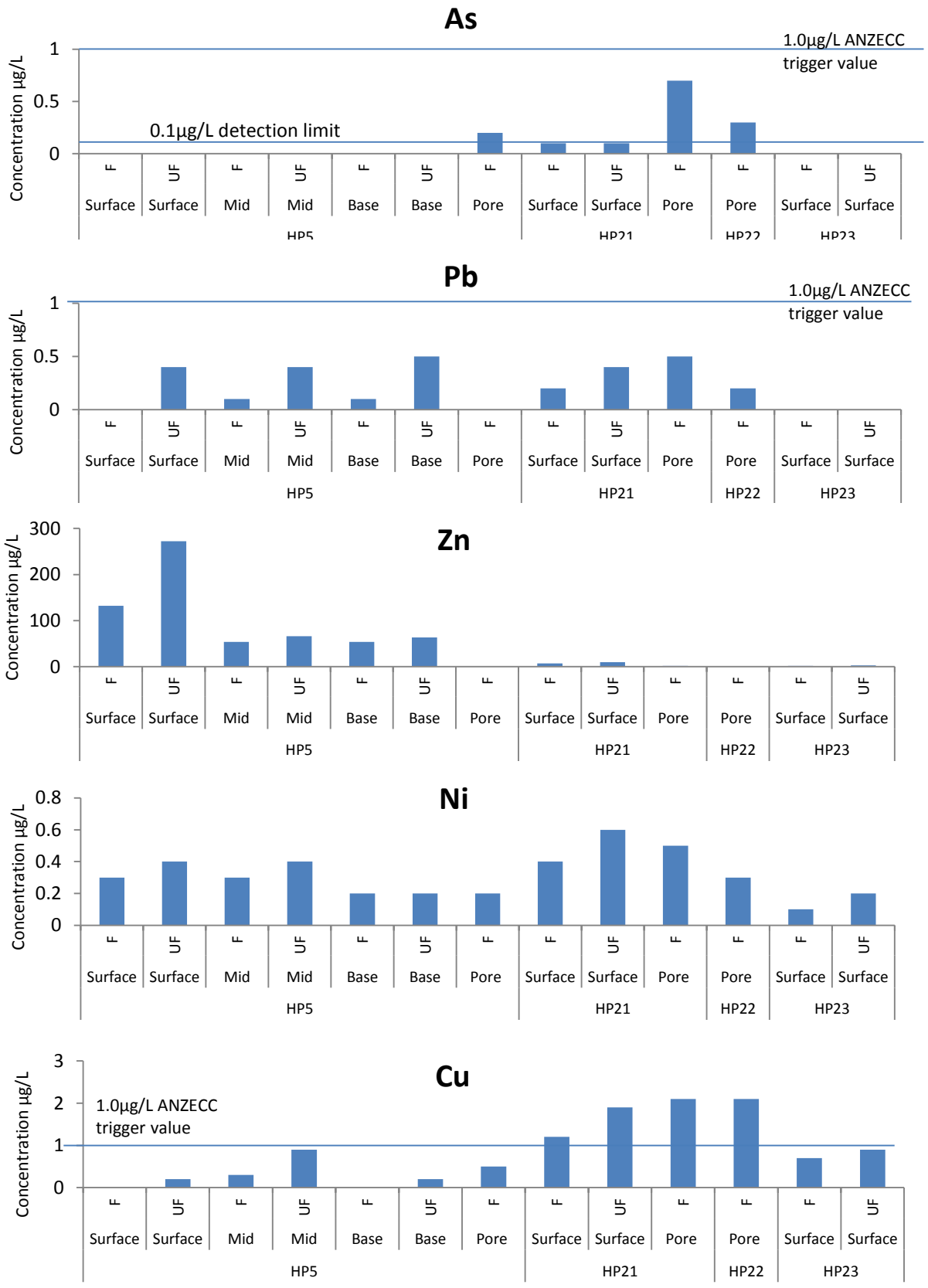


Figure 27 - Trace elements in HP water and porewater samples showing dissolved (f) and total (uf) concentrations and the ANZECC 99% trigger value

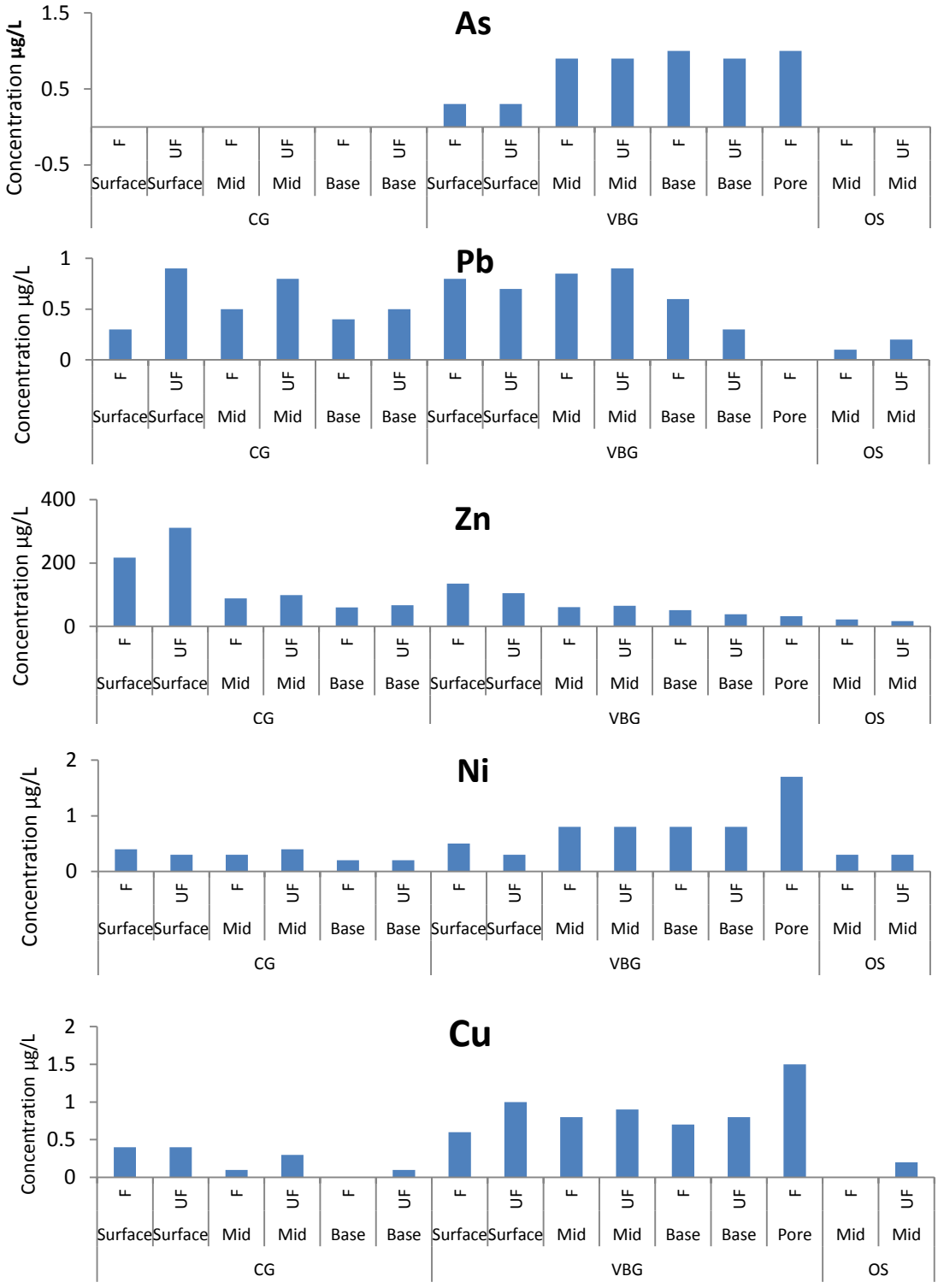


Figure 28 - Trace elements in control sites, water and porewater samples, showing dissolved (f) and total (uf) concentrations.

3.1.5 Sulphide

Sulphide was not detected in any samples.

3.1.6 Nutrients

All water samples were analysed for DRP and NO_x-N, see Appendix 3 for full data set. NO_x-N varies little with depth in water profiles (average 20µg/L) across all Greywater Gully sites, HP5 and in Control Gully (Figure 29). The recently flooded sites (HP21, HP22 and HP23) had higher NO_x-N concentrations than other lake waters (average 43µg/L). NO_x-N concentrations in VBG were significantly higher than all other lake water samples and also increased with depth (Figure 29).

Porewater samples contained higher concentrations of NO_x-N than lake waters, porewater concentrations ranged from 15µg/L to 676µg/L in Greywater Gully, and 936µg/L in VBG (Figure 29).

DRP was below the detection limit in 19/40 samples, and had an average concentration of 2µg/L throughout all water and porewater samples where it was detected (Figure 29). DRP was found at an anomalously high concentration of 940µg/L in the porewater sample from GW6.

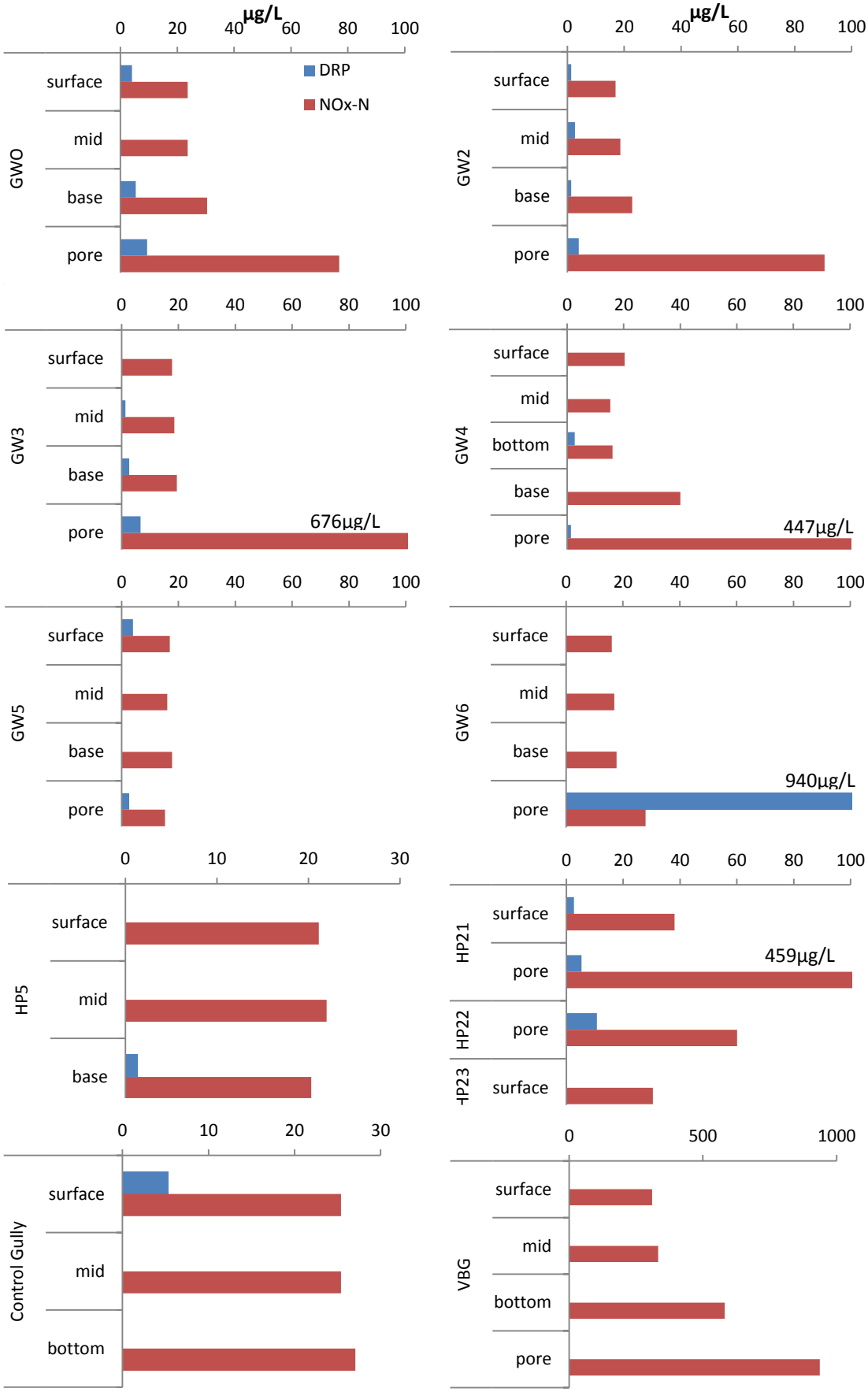


Figure 29 - DRP and NO_x-N concentrations for all water samples.

3.1.7 Volatile Organic Compounds

Of the 64 individual compounds analysed, only styrene, acetone and bromoform were detected (see Appendix 4 for full list of VOCs). Styrene was detected in most samples at concentrations ranging between 0.6-1.9µg/L. Acetone was detected in one basal water sample and two porewater samples between 50-140µg/L. Bromoform ($CHBr_3$) was only detected in basal waters along Greywater Gully and in one porewater sample (GW5). Both styrene and bromoform were measured at higher concentrations in basal waters than in porewaters at every site analysed (Table 14, Table 15).

Table 14 - VOC results for basal water samples.

	Styrene	Acetone	Bromoform
	µg/L	µg/L	µg/L
Guideline[1]	20	-	100
GW0	1.7	<50	<0.5
GW2	NS	NS	NS
GW3	1.5	<50	1.8
GW4*	1.4	<50	1.8
GW4*	1.9	<50	1.8
GW5	1.5	<50	1.8
GW6	2.0	<50	1.6
HP21	0.6	50	<0.5
HP5	<0.5	<50	<0.5
VBG	1.4	<50	<0.5
CG	1.0	<50	<0.5

NS - Not sampled. * - Two basal water samples taken, refer Table 2. [1]- Guideline value from the World Health Organisation (WHO, 2004)

Table 15 - VOC results for porewater samples

	Styrene	Acetone	Bromoform
	µg/L	µg/L	µg/L
Guideline[1]	20	-	100
GW0	0.7	140	<0.5
GW2	0.95	<50	<0.5
GW3	1.3	70	<0.5
GW4	1.1	<50	<0.5
GW5	<0.5	<50	0.7
GW6	<0.5	<50	<0.5
VBG	0.6	<50	<0.5
CG	0.5	150	<0.5

[1]- Guideline value from the World Health Organisation (WHO, 2004)

3.1.8 Total Organic Carbon

Total organic carbon (TOC) was analysed in basal waters of Greywater Gully, HP21, and the control sites. TOC concentrations ranged from 0.8g/m^3 to 2.0g/m^3 in Greywater Gully, was were below detection limit in HP21, and ranged between 0.8-3.6g/m^3 in control samples (Table 16).

Table 16 - TOC results for basal water samples.

	GW0	GW2	GW3	GW4	GW5	GW6	HP21	VBG	CG
TOC g/m^3	0.8	1.1	2.0	1.3	1.9	1.5	<0.5	3.6	0.8

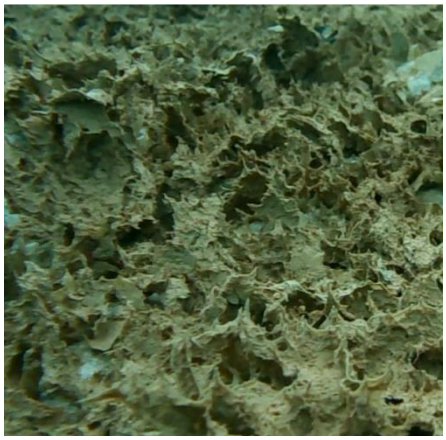
3.2 Cyanobacterial Observations

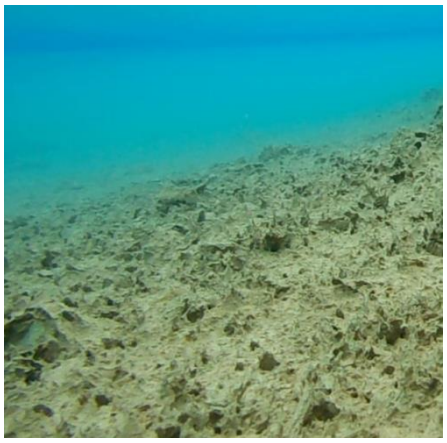
Cyanobacterial mats were observed at 5 sites; one instance on recently inundated soil (Figure 30) and four from sites under approximately 3m water (Figure 31). The four sites under water were GW0, GW4, GW5, and VBG.

There was strong growth of cyanobacterial mats in all of the sites photographed, with greater growth observed in sites GW4 and GW5. There were no obvious signs of inhibited growth (Figure 31). Site GW5 (Figure 31c) showed signs of mat 'lift-off'. This is common in healthy cyanobacterial mats under ice in shallow water and is caused by entrapment of gas in the mat causing increased buoyancy (Hawes & Schwarz, 1999).

Figure 30 - Cyanobacterial mat growing on sediment on the edge of HP21, photographed area approximately 30cm x 30cm .

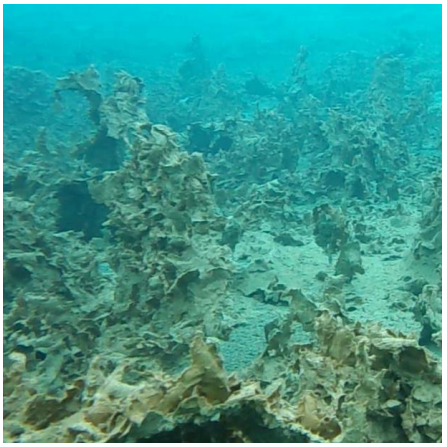
a.





b.

c.



d.

Figure 31 - Underwater camera observations of cyanobacterial mat growth at GW0 (a), GW4 (b), GW5 (c) and VBG (d).

3.3 Soils and Sediments

The former Vanda Station footprint lies on a low lying island approximately 130m long by 40m wide at its widest point. The island rises no more than approximately 1.5m above the current lake level and remains at risk of immediate inundation.

3.3.1 Physical Contaminants and Site Descriptions

Litter and debris was observed and some was collected from the former station island and the helicopter pads for removal and disposal at Scott Base. This debris included batteries (Figure 32), wood chips, nail and screws, pain flecks, and painted stones. A total of 500g of debris was removed, noting that we were not actively searching for debris and simply collected obvious items close to sampling sites. The former helicopter pad and the survey marker “Astro - A” are marked with orange painted rocks. These rocks lie close to lake level will soon be submerged (Figure 18). Additionally, approximately 20 orange painted rocks lie at the current helicopter pad adjacent to the Vanda Huts.

Figure 32 - Battery found in the soil near site HP23.

Figure 33 - Discolouration of the soil at site HP20. This site smelled strongly of hydrocarbons.

The sites HP10 and HP20 were identified as previous fuel spill sites as the soil surface was discoloured and had a strong hydrocarbon smell (Figure 33). The soil in the excavated pits was damp approximately 45cm (HP10) and 25cm (HP20) below the surface. The area affected at each of the two sites is 40cm x 40cm. HP24 was a surface sample from the former helicopter pad nearest to the station. There were no observable fuel residues present and no areas had any perceivable smell. CG was a surface sample in Control Gully (Figure 10) and this site had very similar surrounding geology to the former station island with gneiss/granite bedrock.

3.3.2 Trace Element Contaminants

Soils from the footprint of the former station, and sediments from flooded sites were analysed for trace elements (Table 17). Most trace elements were not elevated (i.e. >1.25 - 1.5) above concentrations measured in CGS (Table 17). The most common trace elements found at elevated concentrations was Zn (maximum concentration 158mg/kg), and Pb (maximum concentration 98.16mg/kg) in the dry HP sites. Both Zn and Pb exceed the ANZECC low trigger value in three samples (Table 17). Results for Zn and Pb in soil profiles from HP10 and HP20 are shown in Figure 34 (HP10) and Figure 35 (HP20) to highlight variation in concentration with increasing depth.

Silver was elevated in soil samples from all depths at site HP20 compared to the CGS control sample. Two of these samples also exceeded the low trigger value from the ANZECC guidelines.

The low guideline value for Cu was exceeded in all samples including controls, and Ni in 7/13 samples despite neither being elevated compared to control samples.

Elevated concentrations are illustrated in Figure 36 where trace element concentrations are plotted against a function of Fe% in the soil matrix. In these figures elevated element concentrations are clearly evident. Vanadium (maximum 58.9mg/kg), Cu (maximum 38.6mg/kg), Cd (maximum 0.6mg/kg) and Pb (maximum 16.3mg/kg) are elevated in some flooded sediment samples.

The two guideline values in Table 17 are from the ANZECC guidelines (ANZECC, 2000), the low value represents the concentration at which contaminants become toxic to benthic organisms and the high value where acute effects are seen. These guidelines were developed for sediment quality in temperate regions, their use here is to assess the significance of contaminants found.

Table 17 - Trace element results in sediment and soil samples as determined from acid digestion. Highlighted results indicate that the concentration is 1.25x (green) and 1.5x (blue) the relevant control site. All results in mg/kg.

	As	Ag	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
						mg/kg						
Guideline												
Low	6	1	0.6	-	26	16	-	460	16	31	-	120
Severe	33	3.7	10	-	110	110	-	1110	75	250	-	820
Sediment												
VBG - control	1.1	0.6	0.2	10	18.8	26.8	21854	309	16.2	3.7	39.2	40.7
GW5	1.2	0.6	0.1	10.4	16.9	36	22608	299	17.7	4.3	58.9	39.6
HP21	1	0.4	0.6	9.2	13.1	38.6	19067	236	17.8	16.3	48.6	41.1
HP22	<0.1	<0.1	NA*	6.2	7.8	25.1	11904	151	11.9	13.7	29.9	14.7
Soils												
HP 10 Surface	1.1	0.4	<0.1	10.9	15	39.9	22957	304	20	7.2	54.3	43.5
HP 10 15cm	0.4	0.4	NA*	10.6	14.1	38.5	21039	247	21.5	4.6	60.9	37.1
HP 10 30cm	0.2	0.2	NA*	8	12.1	33.3	16203	211	15.3	6.2	28.8	26.2
HP 10 45cm	0.2	0.2	NA*	10.2	12.8	38.5	19840	239	18	7.2	41	32.1
HP 20 Surface	1.7	1.0	0.3	7.7	14.3	34.7	16433	208	15.5	98.2	36.3	142.1
HP 20 15cm	1	1.0	NA*	7.5	12.5	30.8	18244	247	13.6	35.9	40.9	158.2
HP 20 25cm	0.9	0.9	NA*	8.1	11.8	31.6	19099	265	14.7	35.8	41.7	117.4
HP24	0.5	0.5	NA*	6.7	8.8	31.23	13703	141	14.8	27.7	51.7	21
CGS - control	1.8	0.6	<0.1	9.6	12.4	36.6	20912	244	17.3	4.4	72.5	26.6

NA* - some Cd results are not available due to cross contamination of samples during digestion. Cd results presented were obtained through retesting from additional samples.

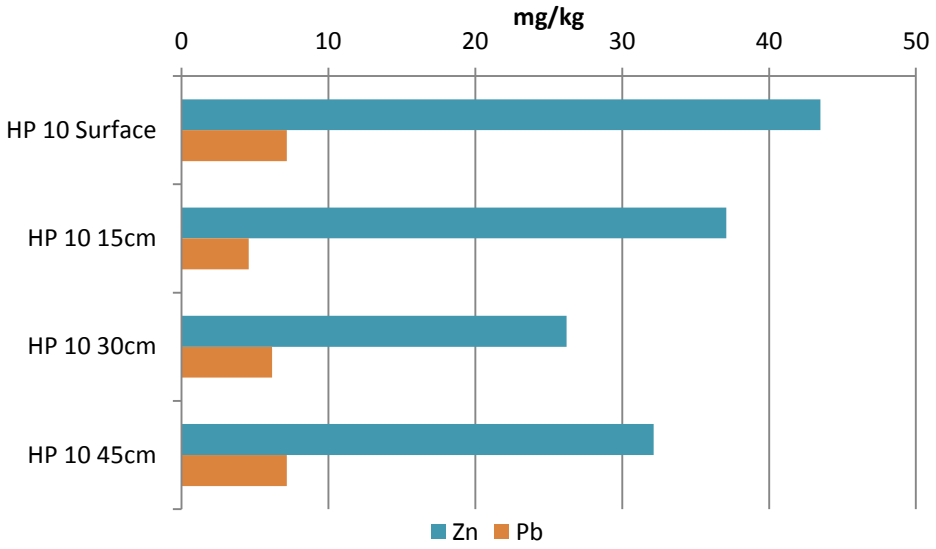


Figure 34 - Lead and zinc concentrations in the soil profile from HP10.

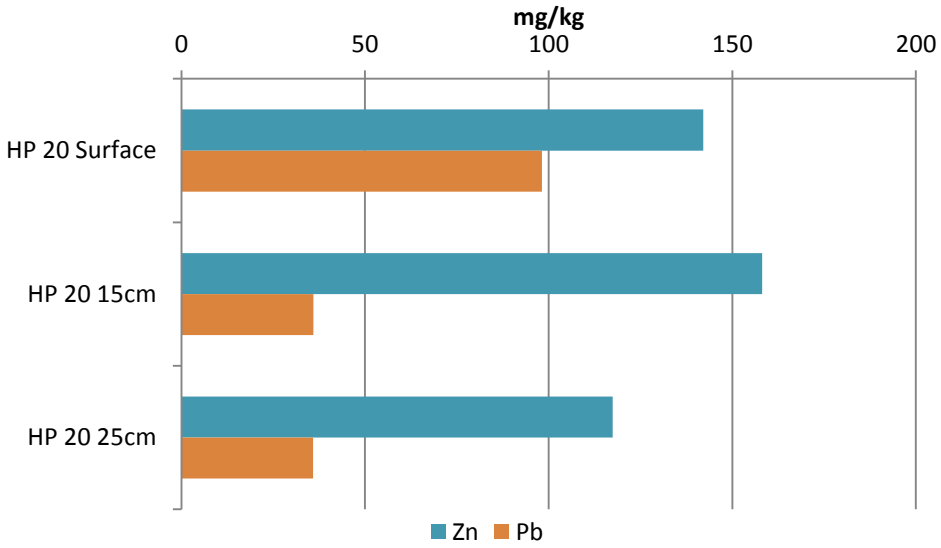


Figure 35 - Pb and Zn concentrations in the soil profile from HP20.

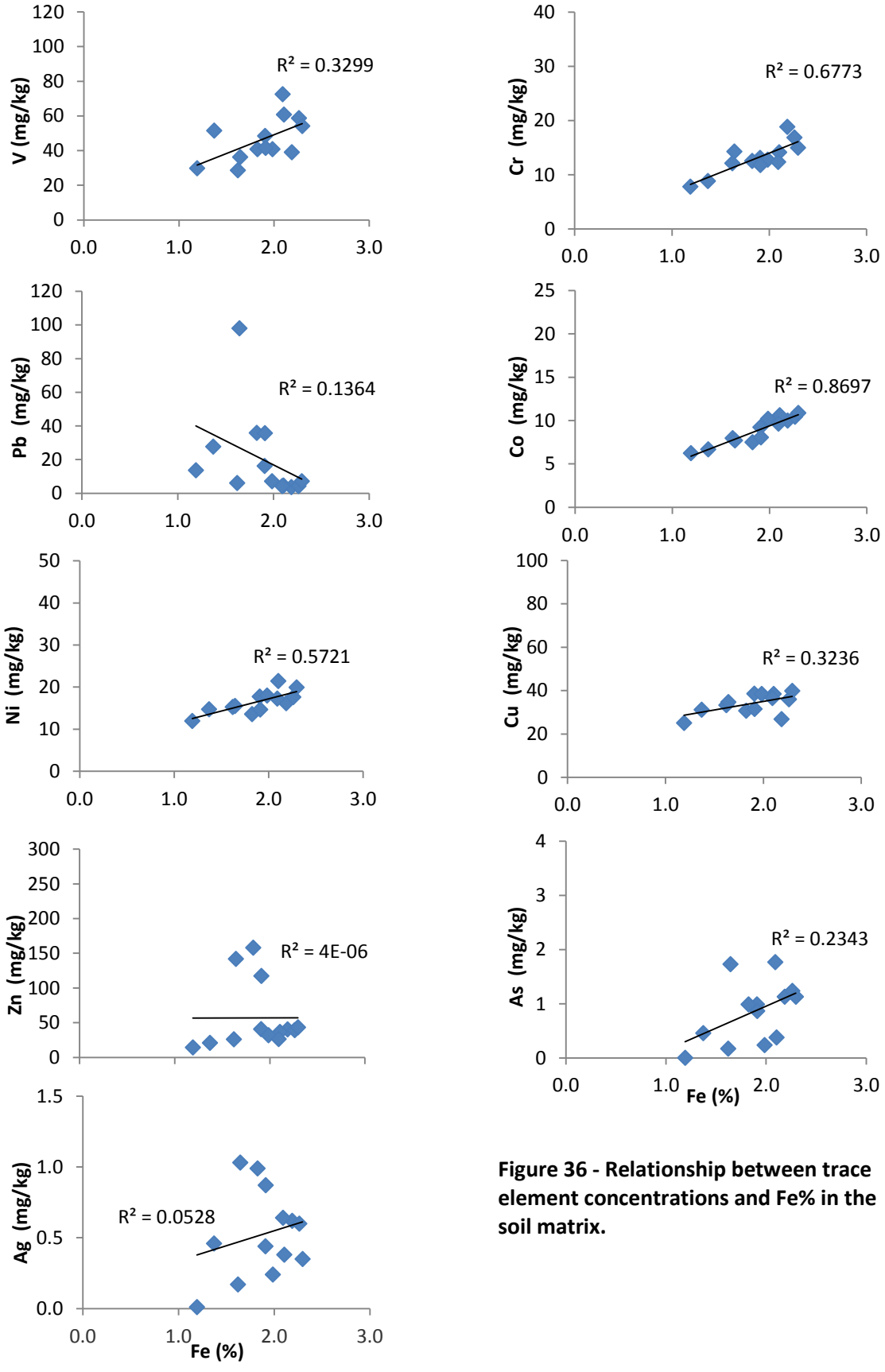


Figure 36 - Relationship between trace element concentrations and Fe% in the soil matrix.

3.3.3 Hydrocarbon Contaminants

Hydrocarbons were not detected in any of the sediment samples or in the surface soil samples from HP24 and CG (Table 18). High concentrations of TPH, particularly for the C15-36 chain lengths, were measured in HP10 and HP20 soil profiles. At site HP10, TPH contamination consisted entirely of hydrocarbons of C15-36 chain length decreasing in concentration with depth (Figure 37). HP20, conversely, contained both C10-14 and C15-36 chain length hydrocarbons. Petroleum hydrocarbon concentrations at HP20 increase with depth from 7000mg/kg at the surface to 8900mg/kg at the bottom of the pit.

Table 18 - Total Petroleum Hydrocarbon results for sediment and soil samples, results in mg/kg.

Sample	TPH (C7-C9)	TPH (C10-C14)	TPH (C15-C36)	TPH (Total)
Sediments				
VBG - Control	<14	<30	<60	<100
GW5	<8	<20	<40	<70
HP21	<8	<20	<40	<70
HP22	<8	<20	<40	<70
Soils				
CG - Control	<8	<20	<40	<70
HP10 - Surface	<8	<20	2,400	2,400
- 15cm	<8	<20	1,620	1,620
- 30cm	<8	<20	300	300
- 45cm	<8	<20	182	182
HP20 - Surface	<8	120	6,800	7,000
- 15cm	9	1,090	7,200	8,300
- 25cm	9	2,300	6,600	8,900
HP24 - Surface	<8	<20	<40	<70

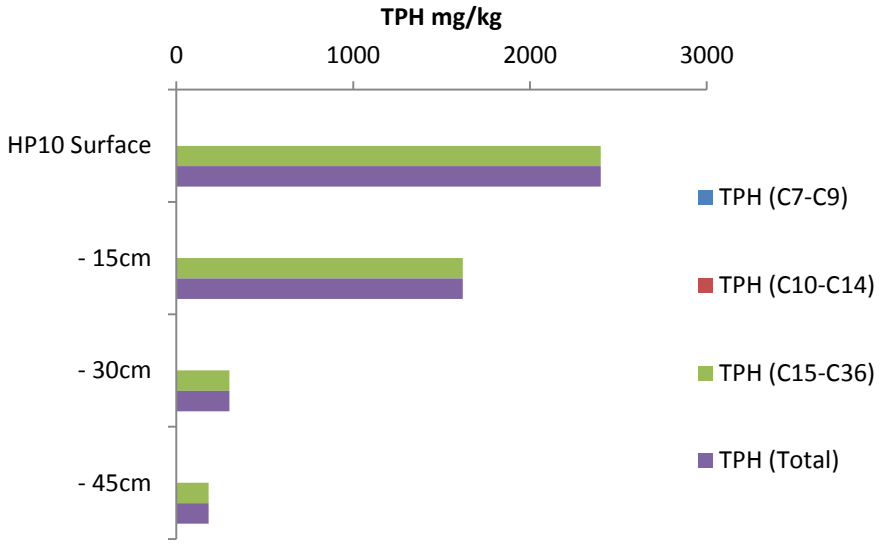


Figure 37 - Fuel contamination in the soil profile of HP10.

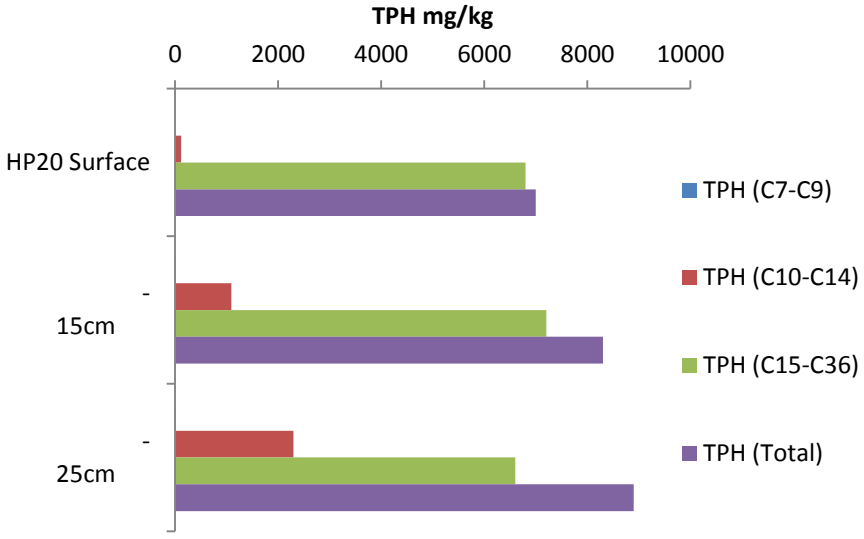


Figure 38 - Fuel contamination in the soil profile of HP20.

3.3.4 TCLP leaching

Trace Elements

Water and acetic acid leachates of all of the dry soils were analysed for trace elements (see Appendix 5 for full dataset) after using the TCLP procedure to simulate the effects of flooding. Water leachates simulate normal leaching into lake waters and acetic acid leachates simulate what might be expected under lower pH, organic-rich conditions such as beneath cyanobacterial mats.

The trace elements Ni, Fe, and Co showed very little variation from control sites (<25%), and Ag was below detection limit in all samples. The greatest concentration in leachates (acetic, water) of Cr (28.3µg/L, 6.8µg/L), Mn (2112µg/L, 797µg/L), Pb (541µg/L, 237µg/L), As (36.5µg/L, 5.8µg/L), Cd (8µg/L, 3.7µg/L), Zn (4813µg/L, 1806µg/L) and Cu (250µg/L, 125µg/L) were all from the site HP20 at varying depths in the soil profile. HP10 only showed elevated Zn in the surface sample.

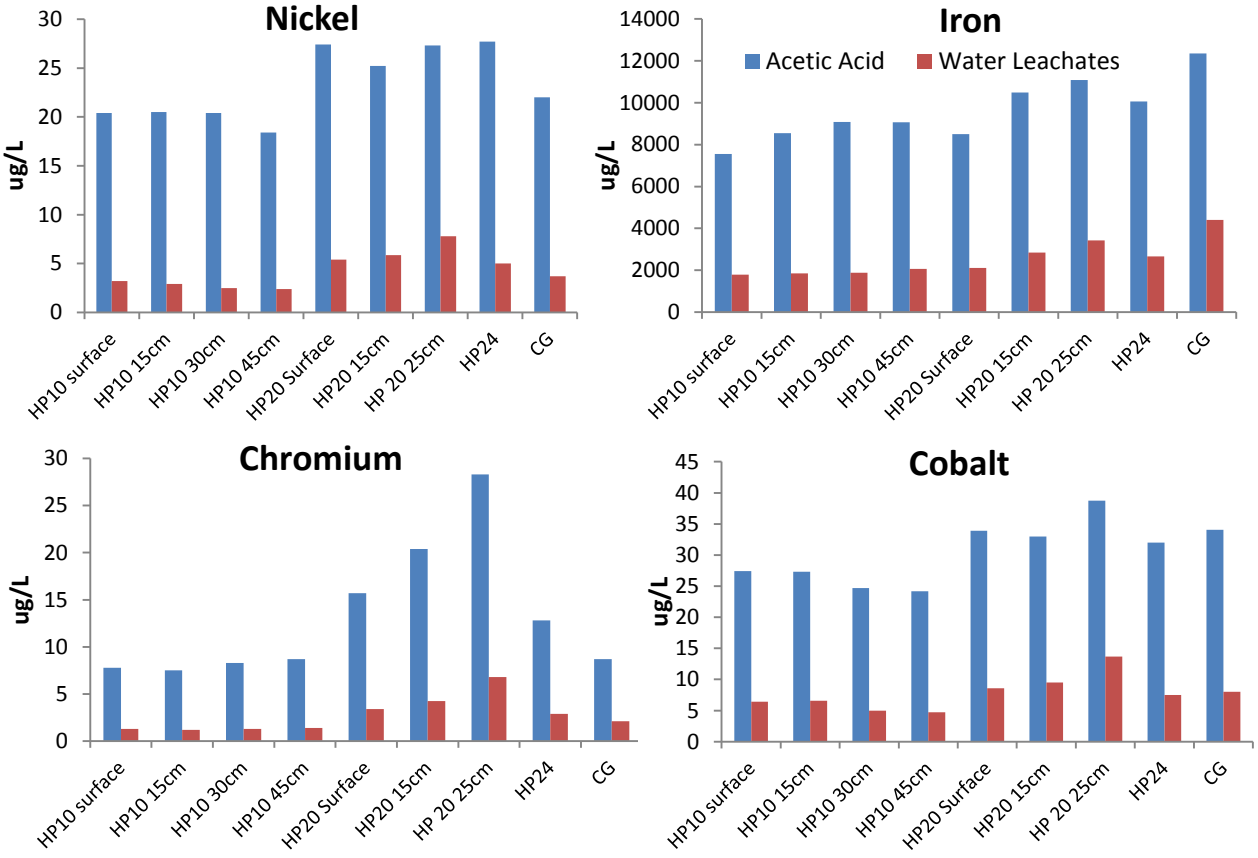


Figure 39 - Leachate concentrations of Ni, Fe, Cr and Co from dry soil samples.

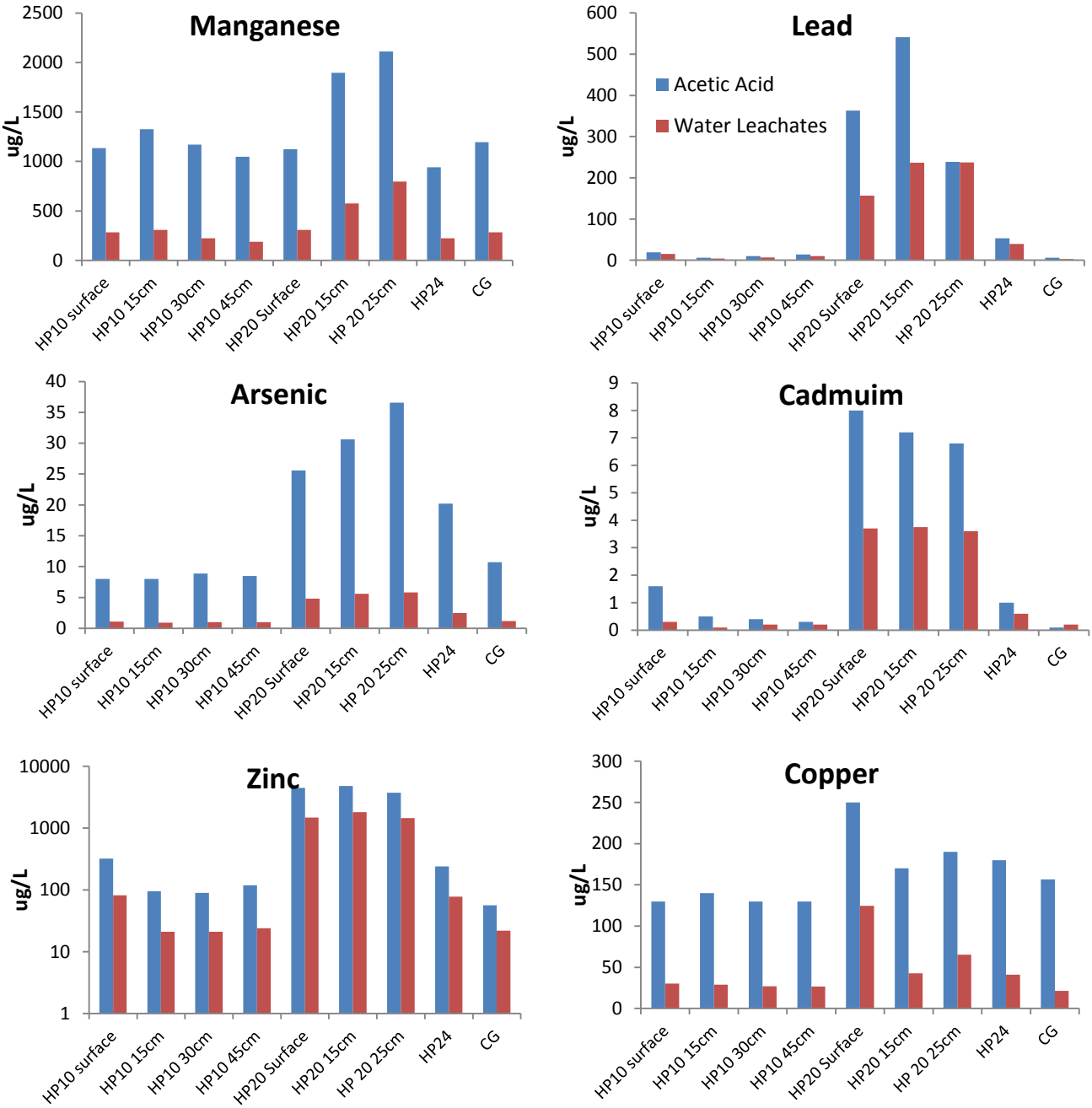


Figure 40 - Leachate concentrations of Mn, Pb, As, Cd, Zn and Cu from dry soil samples.

PAH's

In addition to TPH analysis, acetic acid leachates from HP10, H20, and CGS were analysed for PAHs. The HP20 (25cm sample) leachate contained the PAH naphthalene at 0.0008g/m^3. No other PAH's were detected in any sample. This sample did not exceed the ANZECC 99% guideline value of 0.0025g/m^3.

Chapter 4 - Discussion

4.1 Residual Contamination in Flooded Sites

Vanda Station was fully decommissioned in 1994, extensive remediation of the site was carried out during this time (Waterhouse, 1997). Assessments of environmental effects and studies characterising residual contamination followed this process (Aislabie *et al.*, 1999; Hawes *et al.*, 1999; Sheppard *et al.*, 1994; Webster *et al.*, 2003). These studies identified trace element, nutrient and hydrocarbon pollutants in the soils of Greywater Gully, the main helicopter pads and on the former Station footprint itself.

Greywater Gully was first flooded in the early 2000's; the gully is now completely submerged with its deepest point at approximately 3.5m. The main helicopter pads (HP21-23) lie under approximately 15cm of water and have only recently been flooded, and the Station footprint remains approximately 1m above the lake's surface as measured in this study. This study has determined what, if any, residual contaminants are entering the water column, and whether there are observable effects on benthic cyanobacterial mats.

This study focussed on measuring contaminants identified in prior studies in the water column above, the now flooded, previously monitored soil sites. As these sites are flooded, the locations of the monitored sites in this study not accurately determined and some error exists in the location of previously monitored Greywater Gully sites. However, current sites ensure a good representation of the Gully is made in this assessment. The recently flooded HP21, HP22, and HP23 sites were easily identified, though actual sediment sampling site may differ. The site HP5 is unlikely to be above the previously monitored site, so comparison with previously assessments is not possible.

4.1.1 Trace Elements

Trace element concentrations in the soil and suprapermafrost fluids were last characterised at the former Vanda Station site in 1997 (Webster *et al.*, 2003). The comparison between concentrations in the soil and suprapermafrost fluids in 1997 and overlying lake water in 2014 allows for an assessment of the release of contaminants into Lake Vanda.

Zinc was measured at higher concentrations at the surface of the water column with a decreasing concentration with depth, in most of the water profiles sampled. This trend has been reported previously in Lake Vanda, results in this study align with an expected concentration range (Webster-Brown & Webster, 2007). High surface concentrations of Zn is due to, currently unknown, natural chemical processes in Lake Vanda (Webster-Brown & Webster, 2007; Webster, 1994). Zinc may also be introduced to samples from cross contamination, however care was taken to ensure this didn't happen. Zinc concentrations in this study do not appear to be from residual contamination, as there is no variation between affected sites and controls, and concentrations are lower in basal and porewaters where contaminants would have been released. Instead, the majority of Zn measured in water samples in this study, are likely to be of a natural origin.

Copper measured in Greywater Gully water samples were similar to controls, and concentrations in the HP sites were slightly elevated. Concentrations of Cu measured in this study reflect the natural concentration range of Cu previously identified (0.7-2.2µg/L) (Green *et al.*, 1986) in the surface waters of Lake Vanda, and 0.4-0.6µg/L in the Onyx River inflows (Green *et al.*, 1989). Water samples from HP21 and HP22 had elevated Cu concentrations relative to the controls, this location had previously been monitored with no significantly elevated copper found in the soils (Webster *et al.*, 2003). Elevated copper concentrations in this location may be the result of cryoconcentration in the shallow embayment, or reflect residual Cu concentrations unidentified in previous studies.

For all other trace elements, the measured concentrations in the water column or porewater from both Greywater Gully sites and the helicopter pad (HP) sites were not elevated relative to control sites. Anomalously high concentrations of Fe were measured in HP21 and GW0 water samples. These high concentrations may reflect suspended sediment inclusion in the sample as both samples were taken close to sediment. Iron dissolution from sediment into samples may contribute to these high results. Porewater samples were filtered immediately which may explain the lack of high Fe concentrations in porewater samples from these sites.

Site GW5 sediments, lying at the deepest point in the gully, was analysed for trace elements. Concentrations of V and Cu were elevated relative to the control site sediment (VBG). These concentrations are lower than the unflooded control site (CGS). No other trace element was elevated at GW5. Sediments from HP21 and HP22 contained elevated Cu, Pb and Cd relative to the control. Cu, although elevated to the VBG control, was not significantly higher than CGS. The concentrations of Cu in the soils may reflect the natural concentration in the soils of the Wright Valley, as elevated copper was not reported in previous studies at Vanda Station (Webster *et al.*, 2003).

Lead and Cd in sediments may be attributed to the use of paints containing Pb and Cd pigments on rocks used to mark the helicopter pads, the use of lead based fuels, or residues from batteries (Sheppard *et al.*, 1994; Waterhouse, 1997). These helicopter pads also housed fuel drums, and contaminated soil and ice was stored here following a minor fuel spill on the surface of Lake Vanda (Sheppard *et al.*, 1994).

Cadmium concentrations in sediments at HP21 and HP22 were 0.58mg/kg and were in the lower range of previously attained results (Sheppard *et al.*, 1994; Webster *et al.*, 2003), and within guidelines for sediment quality (low trigger - 1.5mg/kg) (ANZECC, 2000).

Lead results are higher than previously monitored at HP21 and HP22 (Webster *et al.*, 2003). Concentrations of 16.3mg/kg and 13.7mg/kg were measured at these sites, well above the control results of 3.7mg/kg (VBG) and 4.4mg/kg (CGS). These concentrations are below the low level trigger guideline of 50mg/kg (ANZECC, 2000).

Suprapermafrost fluids sampled in 1997 contained elevated concentrations of Cu, Ni, Co, Pb and Zn (Webster *et al.*, 2003), these results are summarised in Table 19. The release of contaminants from these fluids into flooding lake water was of concern as they could cause increased localised trace element concentrations. Suprapermafrost fluids have a very high salinity (3800-10500µS/cm), and lie beneath 30-60cm soil (Webster *et al.*, 2003). During flooding, fresh water occupying pore spaces in the soil is unlikely to mix with the SPF, which has a higher density as the solute gradient is very high, therefore limiting trace element transfer (Webster *et al.*, 2003).

Table 19 - Maximum dissolved concentrations of trace elements in Greywater Gully SPF results from Webster *et al* (2003) and porewater samples in this study.

		Pb	Zn	Cd	Ni	Co	Cu	Ag	As	Cr	Mn	Fe
1997 SPF	µg/L	4.4	17	1.7	99	53	25	0.1	NT	NT	2490	250
2014 Porewater	µg/L	0.5	30	<DL	3.9	2.3	1.1	<DL	1.2	1.0	1888	58

NT - Not tested for in Webster et al's (2003) study.

There is very little evidence for large scale contamination of Lake waters from residual contaminants in the sediment or SPF, and little mixing from sediments. The very high Mn result in this study however, is from the same vicinity as in Webster *et al* (2003) and may indicate some degree of localised porewater mixing with SPF (Table 19). The release of contaminants from the suprapermafrost fluids is unlikely to have had a large effect in Greywater Gully. Maximum

concentrations found in the water and porewaters in Greywater Gully fall below the 95% threshold in the ANZECC guidelines for all trace elements except for Zn.

The site HP5 in this study is unlikely to be the same site as previously monitored, therefore changes in contaminant concentrations or environmental effects cannot be assessed. There are no measurable concentrations of contaminants in the water of HP5 or nearby OS. This may indicate that any released contaminant is not detectable in the main waterbody of Lake Vanda.

4.1.2 Nutrients

NO_x-N (average 20µg/L) and DRP concentrations (average 1µg/L) in the water column in Greywater Gully and HP5 are what would be expected in Lake Vanda. Inputs of nutrients to Lake Vanda vary. Estimates of NO_x-N concentrations in Onyx River inflows range between 8.26µg/L (Canfield & Green, 1985) and 12.04µg/L (Green *et al.*, 2005). With concentrative processes active in the lake (Green & Canfield, 1984), and similar NO_x-N concentrations in the control sites (average 26µg/L), there appears to be no enrichment of NO_x-N in the water of Greywater Gully or HP5. Cryoconcentrative processes are highlighted in the control site VBG where NO_x-N concentrations are higher than at other sites and increase with conductivity (r^2 0.8107).

Higher concentrations of NO_x-N were measured in the porewaters of GW0-GW4, HP21 and VBG, with concentrations ranging from 77µg/L to 937µg/L. Hawes *et al* (1999) analysed lake water extractable nutrients from soils in Greywater Gully and Control Gully and found concentrations ranging from 180-610µg NO_3-N/kg soil. Porewaters in this study results represent this range of NO_3-N except VBG where cryoconcentrative process are likely to also have an effect. Sites GW5, GW6 and HP22 showed no elevated NO_3-N results, these samples are most likely to be lake water rather than porewater due lake water drawdown during porewater sampling (I. Hawes, personal communication 8/12/2015).

DRP was present in most porewater samples and not in control samples, potentially indicating residual concentrations or chemical weathering of sediment bound phosphates (Green *et al.*, 2005). Average DRP concentrations in the water column was 1µg/L, and 5µg/L in the porewater. The high result from GW6 pore (940µg/L) may either represent a concentrated pocket of residual phosphate contamination or be erroneous as no other sample nearby was similar. Natural DRP inputs to Lake Vanda from Onyx River range between 3.7µg/L (reported as phosphate ion) (Canfield & Green, 1985) and 13.3µg/L (DRP) (Green *et al.*, 2005). Most water samples reflect the natural range of DRP in Lake Vanda, and porewater samples may represent residual DRP contamination.

4.1.3 Hydrocarbons

There was no evidence of hydrocarbon contamination remaining at any flooded site. The presence of styrene in most samples, including control sites, may be explained by the presence of styrene in a rubber seal in the water sampling pole used (Bayan, 1990). The lack of variability between samples strengthens this hypothesis. The presence of bromoform in basal water samples, and not in porewater samples, is likely due to the presence of benthic cyanobacterial mats. Some species of cyanobacteria are known to produce methyl halides including bromoform as a by-product of photosynthesis (Manley, 2002). Acetone was detected in the porewaters of CG and GW0 and the HP21 basal water sample. The very low concentrations of acetone in only the control and least affected of the Greywater sites may likely of natural origin (Jacob *et al.*, 2002).

Sediments of HP21, HP22, and GW5 was analysed for TPH. No detectable concentrations of TPH were measured in contrast to Webster *et al* (2003) where a TPH concentration of 2040mg/kg was measured at HP21. As the sampling locations were not exactly aligned, inferring no residual TPH contamination by the lack of detectable TPH in the sediment may not be made.

4.1.4 Organic Carbon and Dissolved Oxygen

The concentrations of TOC in basal waters in Greywater Gully and control sites reflect the natural range in Lake Vanda (Webster *et al.*, 2003). Organic carbon loading can increase the biological oxygen demand creating zones of oxygen depletion (Joyce, Todd, Asmussen, & Leonard, 1985). In all of the sites analysed, DO saturation exceeded 100%, with benthic cyanobacterial growth producing oxygen. There appears to be no residual organic contamination in the sites samples compared to the high TOC (6.8-180mg/kg) as reported in Webster *et al* (2003). Additionally, there appears to be no oxygen depletion in the basal waters along Greywater Gully.

4.1.5 Observed Ecosystem Effects

Previous studies on the residual contamination at Vanda Station expressed concerns for the potential for minor environmental effects including phosphate fertilisation affecting cyanobacterial growth and speciation, and growth inhibition of cyanobacteria due to the toxic effects of trace elements (Hawes *et al.*, 1999; Webster-Brown & Webster, 2007; Webster *et al.*, 2003). Cyanobacteria are the dominant lifeform in Lake Vanda, and form the basis for the entire ecosystem. This study aimed to test the hypothesis that residual contamination is having an effect on cyanobacteria.

The toxicity of trace elements on cyanobacteria in Antarctic freshwater has not been determined. The lowest observed effect concentration (LOEC) for trace elements on Antarctic marine microalgae has been determined (Gissi, Adams, King, & Jolley, 2015). Inhibition of growth starts at concentrations of 300µg/L (Pb), 4.3µg/L (Cu), 910µg/L (Cd), >1070µg/L (Ni), and 1860µg/L (Zn). Trace element concentrations from affected sites in this study were well below these concentrations. This comparison may be used as a rough guideline until more robust effects based research on cyanobacteria is done.

Video cameras were lowered into holes drilled along Greywater Gully to examine the apparent growth of benthic mats (stills depicted in Figure 31). There was strong growth at every site and no apparent inhibition of growth was observed. This is especially important at GW5 where the highest level of contamination was described in previous studies. Cyanobacterial mats at site GW4 and GW5 in Figure 31 exhibit more enhanced growth and mat lift off which is common in healthy cyanobacterial mats in the littoral zone in Antarctic lakes (Hawes & Schwarz, 1999). This apparent heightened growth at GW4 and GW5 may be due to phosphate fertilisation as these sites contained the highest concentrations in prior studies (Sheppard *et al.*, 1994; Webster *et al.*, 2003).

Mat samples taken during this trip to Lake Vanda are in the process of being analysed by I Hawes & S Wood (in preparation) using next generation sequencing (NGS). Their preliminary results indicate no difference in species composition between Greywater Gully and the control samples in VBG.

Being recently inundated, residual contaminants at HP21-23 are not likely to have readily mixed or dispersed into the lake waters; elevated lead concentrations in the sediment at HP21/22 suggests this. The concentrations of trace elements in the water and sediment at these sites fall below the ANZECC guideline trigger values for ecosystem protection. The presence of lead and cadmium bearing paints may cause localised effects on cyanobacteria.

4.2 Residual Contamination on Dry Soils

Very little of the former station lies above the current lake level. Of what is remaining above lake level, two fuel contaminated sites and one other surface site were sampled. The total volume of contaminated soil at HP10 and HP20 is estimated at 0.15m^3. Additional contaminated soil may still exist, but locating non-fuel related contaminated sites proved difficult.

4.2.1 Trace Elements

Vanadium, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, As and Pb were detected in the soil profiles at the three sampling sites at the former Vanda Station site. The concentrations of all of these trace elements were not significantly elevated relative to the control site with the exception of Ag, Pb and Zn (Table 17). This is highlighted in Figure 36 where the correlations between individual elements and %Fe give an indication of the natural concentration range of the trace elements. Lead was elevated (>50% higher than control) in 6/8 samples on the former station footprint, Ag in 3/8, and Zn in 4/8 samples. These metals pose an environmental risk, their leaching potential upon flooding was tested and is discussed in Section 4.3.1.

Sediment quality guidelines from the CCME, outlined in the ANZECC guidelines give an indication of acceptable metal concentrations in sediments (ANZECC, 2000). As these soils will soon be submerged and host cyanobacterial life, freshwater sediment guidelines are best suited. Lead (low guideline value - 31mg/kg), Ag (low guideline value - 1mg/kg), and Zn (low guideline value - 120mg/kg) concentrations exceed the ANZECC guideline values in samples from HP20. Copper (guideline value - 16mg/kg), and nickel (guideline value – 16mg/kg) concentrations exceed the ANZECC low guideline value in most samples including the control samples. The toxicity of trace elements, specifically Pb and Zn, has not been formally examined for cyanobacteria in Antarctic fresh water lakes. Hawes *et* al (1999), however, found no inhibition of growth of cyanobacteria on soils containing ~380mg/kg Pb and ~60mg/kg Zn.

Concentrations of Pb measured in the soil in this study (max 98.16mg/kg) were higher than found at any site at the former Vanda Station in Webster *et al* (2003) (max 23mg/kg), and Sheppard *et al* (1994) (max 68mg/kg). Another site, V22 (Sheppard *et al.*, 1994) in close proximity to HP10 and HP20 in this study, had a maximum concentration of 34mg/kg Pb. Although higher than previously monitored, Pb results in this study are what would be expected on fuel contaminated soil and are comparable to similarly contaminated soils at Scott Base (Williams, 2012).

The major sources of anthropogenic Pb in Antarctica are tetraethyl-lead in fuels, atmospheric deposition from burning leaded fuels, and paints (Claridge *et al.*, 1995; Santos *et al.*, 2005; Sheppard *et al.*, 1994; Sheppard *et al.*, 2000). Lead based primer paint was used at Vanda Station and these paints also contained Cd and Cr (Sheppard *et al.*, 1994). The absence of elevated concentrations of Cd and Cr in the soil and the presence of fuel residues suggests that the primary source of lead at HP10 and HP20 is from tetraethyl lead in fuel. Site HP24 is located on a former helicopter pad and was most likely contaminated with Pb from exhaust deposition or from fuel discharge to soil. The absence of TPH contaminants on HP24 may suggest atmospheric deposition of Pb. Studies have shown limited natural transport of lead in Antarctic soils with Pb persisting in contaminated sites (Claridge *et al.*, 1995; Sheppard *et al.*, 1993), long term studies into the residence time of Pb in Antarctic soils has not been done.

Zinc was elevated in the surface sample from HP10 (max 43.5mg/kg) and throughout the profile at HP20 (max 158.16mg/kg). Zinc concentrations in the profiles of HP10 and HP20 are higher than previously monitored in the soils at Vanda. The high values obtained at HP20 are similar to concentrations at contaminated sites around Scott Base (Williams, 2012).

Zinc in the environment can introduced from building materials, galvanised metals, lubricant oils, tires, and from fuel storage (Claridge *et al.*, 1995; Wuana & Okieimen, 2011). Zinc at Vanda Station,

and in particular HP20, is likely to have come from fuel storage drums on the edge of the former mess building (see Figure 6) (Sheppard *et al.*, 1994). These galvanised drums sat on the surface of the soil with no protective bund during the occupation of the base. This site also contained high concentrations of TPH (discussed in section 4.3.2).

Elevated silver in soil samples from the HP20 profile may have originated from the disposal of photographic solvents. The disposal of photographic solvents is reported to have occurred (Sheppard *et al.*, 1994; Waterhouse, 1997), the exact location of disposal is largely unknown. Silver was most commonly introduced into the environment at Vanda Station by this process, and the presence at HP20, outside the former mess hall, may reflect this.

4.2.2 Hydrocarbons

Petroleum contamination was identified at both HP10 (maximum TPH 2400mg/kg) and HP20 (maximum TPH 8900mg/kg). The maximum concentration of TPH in HP10 was at the surface decreasing in concentration with depth, and conversely the minimum concentration was at HP20 surface increasing with depth. These concentrations are in a similar range to other documented fuel spill sites in Antarctica (Aislabie, Balks, Foght, & Waterhouse, 2004; Gore, Revill, & Guille, 1999; Green & Nichols, 1995; Webster *et al.*, 2003). Rapid volatilisation of shorter chained hydrocarbons has been noted in the McMurdo Dry Valleys (Webster *et al.*, 2003), and may explain the lack of short chain (c7-c9) hydrocarbons in both spill sites. Migration in soil is limited in longer chained hydrocarbons, and the presence of hydrocarbon degrading bacteria may alleviate the small scale fuel spills at the former Vanda Station (Aislabie *et al.*, 1999; Aislabie *et al.*, 2004).

Petroleum hydrocarbons are toxic to Antarctic mosses and terrestrial algae (Nydahl *et al.*, 2015). The Vanda region does not host these species, however the LOEC can be a useful indicator for the significance of contamination. The LOEC of TPH ranged from 6700mg/kg for the sensitive *Prasiola*

species to 62,900mg/kg for *B. pseudotriquetrum* (Nydahl et al., 2015). The maximum concentration of TPH measured in this study is at the lowest end of this range, observed environmental effects on biota (should it exist here) would still be at a minimum.

4.2.3 Physical Debris

During fieldwork, approximately 500g of rubbish was collected. This was comprised of wood chips, nails, paint flakes and batteries (Figure 32). Batteries used in the late 1980's were predominately Ni-Cd and Zn-C, and are a small but very concentrated source of contaminants. Rubbish on the site represents the most obvious contamination, it is both aesthetically displeasing and contain sources of trace element contaminants. As the collection of rubbish was not a priority during fieldwork, and rubbish was only collected close to sampling locations, the total amount remaining is likely to be much higher than this 500g collected.

4.3 Vulnerability of Lake Vanda to Environmental Change

The general chemical nature of Lake Vanda's littoral waters was determined in this study. Previous studies have characterised Lake Vanda's chemical nature and inputs from the Onyx River, e.g. (Angino & Armitage, 1963; Green & Lyons, 2009; Green & Canfield, 1984; Green *et al.*, 1986; Green *et al.*, 1989; Green *et al.*, 2004; Green *et al.*, 2005; Jones & Faure, 1967; Matsubaya *et al.*, 1979).

Analysis in this study show that the surface waters of Lake Vanda are highly oxygenated, have a high pH, and contain low solute concentrations. The general chemistry of Lake Vanda's littoral waters changes rapidly with depth. The pH drops about 0.8 over 1m, the dissolved oxygen content exceeds saturation, and solute content increases. The salinity gradient is particularly strong in regions undergoing cryoconcentration (VBG) and within the sill in Greywater Gully (GW4, GW5) (Figure 24). Throughout Lake Vanda, this trend continues with depth, the pH drops, solute concentration increases and oxygen content decreases (Webster, 1994). The anoxic base of Lake Vanda is held

very stable by a strong chemocline. These deep waters act as a sink for falling precipitates (Green *et al.*, 1989; Webster *et al.*, 2003).

The major ion makeup of Lake Vanda is dominated by the cations Ca^{+} and Na^{+} and the anion Cl^{-} with lesser proportions of HCO_3^{-} (Figure 20, Figure 19). This aligns with previous work characterising the chemical makeup of Lake Vanda's waters and inflows from the Onyx River (Green *et al.*, 2005). Chloride dominates the waters at all depths with its molar dominance increasing with depth (Figure 20); this is characteristic of Wright Valley CaCl brines (Webster, 1994). In oxic upper waters, trace element transport to deeper waters is influenced by adsorption onto Fe and Mn oxides (De Carlo & Green, 2002). Iron and Mn oxide precipitates falling through the water column scavenge trace elements, transporting them to the oxic/anoxic boundary deeper in Lake Vanda (Green *et al.*, 1986; Webster, 1994). Below this boundary, the oxides dissolve and dissolved metals will ultimately be removed from the water as sulphide precipitates, in the anoxic base of the lake (Webster *et al.*, 2003).

Dissolution of contaminants from the soil/sediment can elevate trace element concentrations locally, this process is governed by the redox potential and chemistry in the sediment and water. The redox potential and DO was not measured in the porewaters during this study, however Hawes *et al* (1999) reported that flooded sediments became anoxic between 5-20mm below the surface in Greywater Gully. The precipitation of metal sulphide complexes in the anoxic sediments prevented the release of metal contaminants (Hawes *et al.*, 1999). The absence of sulphide in any porewater sample from this study may reflect the long holding time (APHA, 2007) between sampling and analysis rather than the nature of the sediment/porewater during the time of sampling.

4.3.1 Potential for Contaminant Release from Soils

Lake Vanda's lake level has risen since observations began in 1968 (Figure 3) and the annual rise has varied between -0.3 - 2.1m (Chinn, 1993; McMLTER, 2015). Following Vanda Station's removal, the lake progressively inundated Greywater Gully and the lower helicopter pads. The former station including sampling sites HP10, HP20 and HP24, remain approximately 1m above lake-level and remain at risk of flooding.

Lake Vanda's level rises when inflow volume exceeds ablation losses (Doran *et al.*, 2008). Ablation rates range from 121mm-688mm averaging 326mm/year (data set 1969-1986) (Chinn, 1993), whereas inflow rates have been measured at up to 2106mm (actual lake level rise 1970/71). Ablation on Lake Vanda remains relatively constant and is independent of summer temperatures (Chinn, 1993) whereas higher summer temperatures at the Lower Wright Glacier directly leads to increased inflow into Lake Vanda (Chinn, 1993; Hawes *et al.*, 2013). As lake level and area increases, the input volume required to raise the level increases (Doran *et al.*, 2008). The area of Lake Vanda is currently approximately 7.3km^2 (2014), compared with 5.24km^2 in 1968 ((Chinn, 1993)). This corresponds to an approximate inflow volume of 7.324x10^{6}m^3 (2014) and 5.257x10^{6}m^3 (1968) required increasing the lake's level by 1m over 1 year. This takes into account ablation but assumes no change in area during a 1m level increase.

Based on historical hydrological data (Chinn, 1993; McMLTER, 2015), and predictions for changing climate in McMurdo Sound (Andrew, Joseph, Michael, & David, 2014; Bernstein *et al.*, 2008; Bomblies, McKnight, & Andrews, 2001; Hoffman, Andrew, & Liston, 2014), Lake Vanda is expected to inundate the remainder of the former station footprint. A detailed hydrological model encompassing climate change in the McMurdo Dry Valleys, is however, needed for accurate predictions.

The TCLP analyses predict leaching of trace elements under both a neutral and acidic environment. The results indicate the metals Ni, Fe, Co, Ag and Cu are unlikely to leach from any site in concentrations higher (>25%) than the control site. With little mobilisation and a large dilution factor in Lake Vanda, negligible effects are anticipated. The trace elements Cr, Mn, Pb, As, Cd, Zn and Cu showed higher concentrations in leachates from HP20 than the control site soils (Figure 39, Figure 40).

Trace element concentrations in leachates from HP10 and HP20 are comparable to results obtained from HP10 in 1996 (Webster *et al.*, 2003) with the exception of Pb, Zn and Cu which are an order of magnitude higher in this study. A leaching study of metals from Scott Base on Ross Island yielded similar results to Pb, Zn and Cu (Sheppard *et al.*, 2000), however, soil concentrations were not reported so comparison of results is not possible.

Lead and Zn are the two most likely metals to be mobilised into lake water as the sites flood as they are elevated in the soil and are readily leached. This indicates that the Pb in the soil is organically bound as adsorbed Pb is not readily leached (Sheppard *et al.*, 2000). Concentrations in the leachates exceed the ANZECC freshwater guidelines (at all trigger levels) but are unlikely to cause more than a short term local effect due to the small volume of affected soil and the large dilution factor provided by the lake. Ultimately, leached elements will dissipate into the main waterbody of Lake Vanda and bind with oxides and organic particulates in the water. These precipitates will eventually drop in the water column. As the magnitude of contamination is small, natural chemical processes in Lake Vanda will remove introduced contaminants from the surface waters. The residence times for trace metals in the upper water of Lake Vanda are long compared to open systems (Green *et al.*, 1986), and is analogous to that of the oceans. The mechanism for trace element scavenging and removal

therefore would provide little remediative effects in the instance of a large contamination event (Webster *et al.*, 2003).

4.4 Is further remediation necessary?

From the point of ecosystem protection, the levels of contaminants present in the soil and water at the former Vanda Station and surrounding areas pose only a minor risk of ecosystem effects. This conclusion is based on the concentrations present, the likely leaching of such contaminants, the dilution factor of Lake Vanda and the known effects of contaminants on cyanobacterial growth.

Evidence from Greywater Gully indicates that there are no observable long term environmental effects; this is true also at the recently submerged helicopter pads. This may be extrapolated to say that the contaminated soil found on the station footprint poses little threat to the Lake should it be flooded.

The opportunity for remediation of these two exposed soil sites and the removal of painted rocks from the area exists however, and should be considered. Remediation of former work sites is obligatory under the Madrid Protocol only where the benefits of removing contaminants outweigh the impacts of carrying out remediation (Poland, Riddle, & Zeeb, 2003; Snape *et al.*, 2001). One of the largest remediation efforts was of contaminated sites at Australia's Casey Station. Remediation here was based along provisions in the Madrid Protocol, whereas the protection of the environment was ensured and no adverse effects were generated during remediation (Snape *et al.*, 2001; Stark *et al.*, 2006). This effort was a major success, extensive monitoring and management of the surrounding ecosystems ensured that remediation efforts didn't adversely affect the environment (Stark *et al.*, 2006).

The scale of contaminated land at Vanda Station is very small compared with Casey Station (0.15m^3 - Vanda, 2500m^3 - Casey). This estimate does not account for additional unknown contaminated

areas. Semi-submerged painted rocks at HP21 and Astro-A, along with painted rocks at the Vanda Huts constitute an additional approximate 2-4m^3. The two fuel spill sites may be easily dug to the permafrost as the soil is dry and unfrozen, removal may be easy by hand into bags for removal. Very little disturbance or environmental effects are likely from such an operation, as was seen during the initial remediation effort at Vanda Station (Waterhouse, 1997). The benefits of removing the contaminated soil will likely outweigh any negligible negatives, therefore its removal is recommended.

Chapter 5 - Conclusions and Recommendations

Twenty-five years of occupation at Vanda Station, coupled with relatively poor environmental protection standards by modern standards led to minor contamination of the surrounding land. During the stations decommissioning, extensive remediation removed the majority of contaminated soil. Residual contamination remained at the site however and posed a risk to Lake Vanda should the lake level rise and the site be flooded. Now 21 years following, the station site is largely under water. The extent of residual contamination in exposed soil, and environmental effects in Lake Vanda was re-evaluated.

This study revealed no trace of previously identified contaminants in the lake water. There is no evidence of elevated nutrients, trace elements and organic contaminants in the water along Greywater Gully, the most contaminated part of the site, or in the flooded helicopter pads relative to the concentrations in other parts of Lake Vanda. The lack of detectable contaminant release from sites previously identified as affected may be due to the high density of contaminated suprapermafrost fluids. Additionally, the large dilution factor in Lake Vanda is likely to dissipate contaminants to non-detectable levels.

Observations of benthic algal mats within Greywater Gully indicate healthy and luxurious growth at GW4 and GW5. The hypothesised effects of phosphate fertilisation appears to be affecting cyanobacterial growth at these two sites. Toxic effects of trace elements present was not observed. Sequencing of rRNA genes of cyanobacteria indicates no variation in speciation. My hypothesis: ***Residual contamination at the Vanda Station site continues to affect water quality and cyanobacterial growth near this site*** is rejected. I conclude that residual contamination at the former Vanda Station site is only having a minor perceived effect on cyanobacterial growth in a small area, and not having an observed effect on water quality.

No environmental effects are anticipated in the wider environment of Lake Vanda as there are no observable effects now. The scavenging of metals in the water column and sequestering within sulphide precipitates in the deeper waters will facilitate the natural removal of low level metal contamination in the long term.

Exposed soil on the former stations footprint remains contaminated with hydrocarbons and trace elements at two monitored sites. These sites exhibit concentrations of TPH 8900 mg/kg, Pb 98.16 mg/kg and Zn 158.16 mg/kg. This level of contamination exceeds CCMA sediment guideline values for Pb and Zn and the TPH concentration exceeds the LOEC for Antarctic mosses. The leaching procedure results indicate the potential for localised enrichment of trace elements in the water column once the site floods. Long term environmental effects from this contamination is unlikely due to the low volume of contaminated soil and the large dilution factor in Lake Vanda.

An opportunity to remove the remaining contaminated soil at the former Vanda Station still exists. This process will reduce the risk of these contaminants causing localised environmental effects, as required under The Madrid Protocol. Furthermore, removing remaining contaminated soil, surface debris and painted marker rocks from the valley will remove the potential sources of contaminants without adversely affecting the environment in the process.

5.1 Recommendations

The removal of the painted marker rocks from the vicinity of the Vanda Huts, Astro “A” survey point and HP21 should be carried out prior to flooding. The paint on these rocks contain Pb, Cr and Cd and they are a source of contamination. Additionally, soil from HP10 and HP20 should be excavated and removed, and the soils should be searched for rubbish to be removed. The total volume to be removed will be approximately 2-4 m^3 and the process of removal should create no adverse effects to the environment.

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Appendix 1 - Major Ion Chemistry

			Na	K	Mg	Ca	HCO_3^-	Cl^-	SO_4^{2-}
			mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
GW0	Surface	F	13.9	5.2	4.1	17.6			
		UF	13.4	5.2	4	17.2	65.19	58.73	2.57
	Mid	F	52.2	16.3	20.1	82.5			
		UF	52.1	16.1	20.1	81.4	90.99	232.70	16.81
	Base	F	50.5	15.7	20	80.3			
		UF	51.3	15.3	20	79.9	80.84	256.02	20.47
	Porewater	F	54.3	17.1	20.1	86.1	81.44	261.26	20.95
GW2	Surface	F	10.8	4.1	3.2	13.7			
		UF	10.9	4.1	3.2	13.9	57.14	47.94	1.68
	Mid	F	11.7	4.5	3.4	14.8			
		UF	10.5	4	3.1	13.8	54.23	49.74	2.77
	Base	F	51.2	15.3	20.5	79.8			
		UF	52.3	15.8	21	81.5	93.23	237.40	16.41
	Porewater	F	52.3	17.3	19.3	79.5	78.93	239.21	18.96
GW3	Surface	F	10.3	3.7	3.1	13			
		UF	10.4	3.8	3.2	13.7	53.1	44.13	2.65
	Mid	F	76.3	22.3	30.7	107			
		UF	75.4	22.1	30.3	108.8	75.46	335.00	24.40
	Base	F	73.7	22	29.6	104.9			
		UF	75.5	22	29.7	106.8	91.17	346.69	28.67
	Porewater	F	63.1	17.2	21.5	84	82.1	267.04	21.47
GW4	Surface	F	12.3	3.9	3.6	13.7			
		UF	12.1	3.8	3.6	13.4	48.53	47.63	6.94
	Mid	F	76.8	22.6	30.4	110.1			
		UF	75.4	22.2	30.1	107.5	90.08	337.05	27.80
	Bottom	F	74.9	22.4	30.5	106.9			
		UF	74.4	22	29.8	106	76.84	339.80	26.15
	Base	F	76.2	22.3	30.4	109			
		UF	76.5	22.6	31.1	110	91.96	353.58	29.29
	Porewater	F	153	33	69.2	231.5	121.00	608.51	52.32
GW5	Surface	F	12.7	4.3	3.6	14.3			
		UF	12.9	4.1	3.5	14	53.54	49.56	3.41
	Mid	F	75.9	22.6	30.4	109.6			
		UF	71.7	21.6	29.4	105.8	80.03	338.00	24.90
	Base	F	75	22.2	30.4	107			

			Na mg/L	K mg/L	Mg mg/L	Ca mg/L	HCO_3^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L
		UF	76.4	22.9	30.2	108.2	91.65	350.83	29.04
	Porewater	F	107.9	30.2	41.2	152.4	102.95	450.04	38.00
GW6	Surface	F	9.5	3.7	3	13.1			
		UF	9.9	3.8	3	13.4	50.34	41.88	2.45
	Mid	F	68.6	20.6	27.7	100.2			
		UF	70.2	21.3	28.1	103.3	77.27	335.30	24.29
	Base	F	73.1	21.7	29.3	105.3			
		UF	74.2	22.4	30.1	108.3	91.33	348.07	28.79
	Porewater	F	72.9	24.3	27.8	106.2	89.73	334.01	27.52
HP5	Surface	F	14.5	5.4	4.7	19.3			
		UF	14.5	5.3	4.6	19.2	54.92	62.21	3.05
	Mid	F	19.2	6.6	7	27.9			
		UF	19.2	6.7	7	27.9	60.65	78.81	4.46
	Base	F	30.3	9.8	11.7	46.5			
		UF	30.6	9.9	11.9	47.3	74.08	134.70	9.15
	Porewater	F	40.6	14.3	13.6	67.4			
CG	Surface	F	6.1	2.6	1.6	7.1			
		UF	5.9	2.6	1.6	6.9	55.66	34.99	0.50
	Mid	F	51.6	15.9	21.1	82.1			
		UF	51.2	15.7	20.7	80.8	94.62	231.60	16.64
	Base	F	51.1	16.2	20.9	83.1			
		UF	51	15.8	20.7	81.7	93.25	238.20	16.69
	Porewater	F					79.81	246.92	19.65
VBG	Surface	F	116.1	34.6	45.4	175			
		UF	120.4	36.1	46.6	182.7	137.09	581.70	46.12
	Mid	F	321.4	94.3	127.9	494.7			
		UF	322.5	95.7	129.2	495.1	207.35	1366.41	120.80
	Base	F	337.5	99.1	134.6	513.6			
		UF	347.2	99.5	136	519.2	205.11	1396.00	128.57
	Porewater	F	424.9	102.7	183	644	237.81	1633.74	144.95
OS	Mid	F	52.5	16.2	21.3	84.1			
		UF	52.2	16.2	21.4	83.9	80.34	251.61	20.08
HP21	Surface	F	14.4	5.9	3.7	15			
		UF	14.3	5.9	3.7	15	57.42	48.94	5.28
	Porewater	F	56.4	18.8	20.1	64			
HP22	Porewater	F	22.8	10.3	6.1	26.6			
HP23	Surface	F	12.5	5.1	3.2	13.2			
		UF	12.5	5.1	3.2	13.5	53.54	45.43	4.69

Appendix 2 - Water trace elements

			Mn	Fe	Pb	Zn	Cd	Ni	Co	Cu	Ag	As	Mo	Cr
			µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
		DL	1	1	0.1	1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	1
GW0	Surface	F	<DL	<DL	0.2	40	<DL	0.2	<DL	<DL	<DL	<DL	0.3	<DL
		UF	<DL	7	0.2	22	<DL	0.1	<DL	<DL	<DL	<DL	0.3	<DL
	Mid	F	<DL	6	0.7	99	<DL	0.5	<DL	0.6	<DL	0.1	1.9	<DL
		UF	<DL	8	1	87	<DL	0.4	<DL	0.6	<DL	0.1	1.7	<DL
	Base	F	<DL	5	0.1	31	<DL	0.2	<DL	0.1	<DL	0.1	1.7	<DL
		UF	6	239	0.5	33	<DL	0.5	0.2	0.8	<DL	0.1	1.5	<DL
	Porewater	F	<DL	3	<DL	3	<DL	0.3	<DL	0.5	<DL	0.2	2.9	1
GW2	Surface	F	<DL	4	0.3	65	<DL	0.5	<DL	0.9	<DL	<DL	0.4	<DL
		UF	<DL	12	1.1	120	<DL	1.8	<DL	1.1	<DL	<DL	0.2	<DL
	Mid	F	<DL	4	0.4	86	<DL	0.4	<DL	0.9	<DL	<DL	0.3	<DL
		UF	<DL	5	1.2	101	<DL	0.2	<DL	0.4	<DL	<DL	0.3	<DL
	Base	F	<DL	2	0.3	50	<DL	0.3	<DL	0.1	<DL	<DL	1.7	<DL
		UF	<DL	7	0.4	41	<DL	0.3	<DL	0.2	<DL	0.1	1.7	<DL
	Porewater	F	1	1	<DL	1	<DL	0.3	<DL	0.7	<DL	0.2	2.6	<DL
GW 3	Surface	F	<DL	1	0.2	46	<DL	0.2	<DL	0.3	<DL	<DL	0.3	<DL
		UF	<DL	8	1.3	118	<DL	0.4	<DL	0.8	<DL	<DL	0.3	<DL
	Mid	F	<DL	3	0.5	68	<DL	0.6	<DL	1	<DL	0.2	2.7	<DL
		UF	<DL	6	1.1	80	<DL	0.4	<DL	0.7	<DL	0.2	2.5	<DL
	Base	F	<DL	4	0.7	66	<DL	0.4	<DL	0.8	<DL	0.2	2.6	<DL
		UF	<DL	7	0.5	49	<DL	0.3	<DL	0.6	<DL	0.2	2.7	<DL
	Porewater	F	<DL	2	<DL	1	<DL	0.3	<DL	0.4	<DL	0.2	6.9	1
GW 4	Surface	F	<DL	2	0.9	107	<DL	0.8	<DL	0.8	<DL	<DL	0.5	<DL
		UF	<DL	11	1.3	287	<DL	1.5	<DL	1.1	<DL	<DL	0.4	<DL
	Mid	F	<DL	4	0.3	112	<DL	0.5	<DL	0.5	<DL	0.1	2.7	<DL
		UF	<DL	5	0.5	113	<DL	0.5	<DL	0.5	<DL	0.1	2.7	<DL
	Base	F	<DL	3	0.4	64	<DL	0.9	<DL	0.5	<DL	0.2	2.8	<DL
		UF	1	16	1.5	137	<DL	5.4	0.1	0.8	<DL	0.2	2.7	1
	Bottom	F	<DL	31	0.3	52	<DL	0.3	<DL	0.5	<DL	0.2	2.9	<DL
		UF	2	84	1.1	75	<DL	0.7	<DL	0.7	<DL	0.2	2.7	<DL
	Porewater	F	35	5	<DL	30	<DL	0.9	0.1	0.8	<DL	0.3	9.1	<DL
GW 5	Surface	F	<DL	4	0.3	51	<DL	0.6	<DL	0.8	<DL	<DL	0.5	<DL
		UF	<DL	13	0.8	50	<DL	0.7	<DL	1	<DL	<DL	0.3	<DL
	Mid	F	<DL	3	0.3	51	<DL	0.4	<DL	0.5	<DL	0.1	2.7	<DL
		UF	<DL	5	0.3	25	<DL	0.6	<DL	0.5	<DL	0.1	2.7	<DL
	Base	F	<DL	3	0.2	34	<DL	0.3	<DL	0.4	<DL	0.1	2.8	<DL
		UF	<DL	19	0.3	31	<DL	0.4	<DL	0.5	<DL	0.1	2.8	<DL
	Porewater	F	1888	58	0.1	11	<DL	3.9	2.3	0.6	<DL	1.2	14.2	<DL

			Mn	Fe	Pb	Zn	Cd	Ni	Co	Cu	Ag	As	Mo	Cr
			µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
GW6	Surface	F	<DL	3	0.7	55	<DL	0.2	<DL	0.5	<DL	<DL	0.6	<DL
		UF	<DL	1	0.2	33	<DL	0.1	<DL	0.2	<DL	<DL	0.3	<DL
	Mid	F	<DL	2	0.5	61	<DL	0.3	<DL	0.5	<DL	0.1	2.55	<DL
		UF	<DL	4	0.5	33	<DL	0.3	<DL	0.5	<DL	0.1	2.5	<DL
	Base	F	<DL	2	0.4	41	<DL	0.3	<DL	0.5	<DL	0.1	2.7	<DL
		UF	<DL	5	0.5	49	<DL	0.4	<DL	1.3	<DL	0.2	2.7	<DL
	Porewater	F	7	2	0.5	5	<DL	0.5	<DL	1.1	<DL	0.4	4.1	<DL
HP5	Surface	F	<DL	2	<DL	132	<DL	0.3	<DL	<DL	<DL	<DL	0.4	<DL
		UF	<DL	17	0.4	272	<DL	0.4	<DL	0.2	<DL	<DL	0.3	<DL
	Mid	F	<DL	1	0.1	54	<DL	0.3	<DL	0.3	<DL	<DL	0.5	<DL
		UF	<DL	9	0.4	66	<DL	0.4	<DL	0.9	<DL	<DL	0.5	<DL
	Base	F	<DL	2	0.1	54	<DL	0.2	<DL	<DL	<DL	<DL	1	<DL
		UF	<DL	26	0.5	63.5	<DL	0.2	<DL	0.2	<DL	<DL	1	<DL
	Porewater	F	<DL	1	<DL	<DL	<DL	0.2	<DL	0.5	<DL	0.2	6.7	1
CG	Surface	F	<DL	1	0.3	217	<DL	0.4	<DL	0.4	<DL	<DL	0.3	<DL
		UF	<DL	4	0.9	311	<DL	0.3	<DL	0.4	<DL	<DL	0.2	<DL
	Mid	F	<DL	2	0.5	88	<DL	0.3	<DL	0.1	<DL	<DL	1.7	<DL
		UF	<DL	6	0.8	99	<DL	0.4	<DL	0.3	<DL	<DL	1.6	<DL
	Base	F	<DL	2	0.4	60	<DL	0.2	<DL	<DL	<DL	<DL	1.8	<DL
		UF	<DL	6	0.5	67	<DL	0.2	<DL	0.1	<DL	<DL	1.7	<DL
VBG	Surface	F	3	16	0.8	135	<DL	0.5	<DL	0.6	<DL	0.3	4.2	1
		UF	3	30	0.7	105	<DL	0.3	<DL	1	<DL	0.3	4.2	1
	Mid	F	3	10	0.85	61	<DL	0.8	0.1	0.8	<DL	0.9	12.2	3
		UF	3	15	0.9	65	<DL	0.8	0.1	0.9	<DL	0.9	12	3
	Base	F	2	9	0.6	51	<DL	0.8	0.1	0.7	<DL	1	13	3
		UF	2	9	0.3	38	<DL	0.8	0.1	0.8	<DL	0.9	12.9	3
	Porewater	F	36	9	<DL	32	<DL	1.7	0.2	1.5	<DL	1	17.4	4
HP21	Surface	F	2	68	0.2	7	<DL	0.4	<DL	1.2	<DL	0.1	1	<DL
		UF	5	225	0.4	10	<DL	0.6	0.2	1.9	<DL	0.1	0.7	<DL
	Porewater	F	1	3	0.5	2	0.1	0.5	<DL	2.1	<DL	0.7	3.1	<DL
HP22	Porewater	F	2	4	0.2	1	<DL	0.3	<DL	2.1	<DL	0.3	1.5	<DL
HP23	Surface	F	<DL	12	<DL	2	<DL	0.1	<DL	0.7	<DL	<DL	0.6	<DL
	Surface	UF	<DL	23	<DL	3	<DL	0.2	<DL	0.9	<DL	<DL	0.7	<DL
OS	Mid	F	<DL	3	0.1	22	<DL	0.3	<DL	<DL	<DL	<DL	1.7	<DL
		UF	<DL	10	0.2	17	<DL	0.3	<DL	0.2	<DL	<DL	1.7	<DL
IV SRM	Standard		41	99	20.1	72	7.1	61.9	28.8	20	<DL	59.3	122.6	21
Blank	Acid	F	<DL	<DL	<DL	8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Blank	Acid	UF	<DL	<DL	<DL	4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

Appendix 3 - Nutrients

		DRP µg/L	NOx-N µg/L			DRP µg/L	NOx-N µg/L
GWO	surface	4	24	**GW6**	surface	0	16
	mid	0	24		mid	0	17
	base	5	30		base	0	18
	pore	9	77		pore	940	28
GW2	surface	1	17	**CG**	surface	5	25
	mid	3	19		mid	0	25
	base	1	23		bottom	0	27
	pore	4	91	**VBG**	surface	0	310
GW3	surface	0	18		mid	0	332
	mid	1	19		bottom	0	581
	base	3	19		pore	1	937
	pore	7	676	**OS**	mid	0	26
GW4	surface	0	20	**HP5**	surface	0	21
	mid	0	15		mid	0	22
	bottom	3	16		base	1	20
	base	0	40	**HP21**	surface	3	38
	pore	1	447		pore	5	459
GW5	surface	4	17	**HP22**	pore	11	60
	mid	0	16	**HP23**	surface	0	30
	base	0	18				
	pore	3	15				

Appendix 4 - Hydrocarbons

List of VOCs analysed

BTEX	Halogenated Aromatics
Benzene	Bromobenzene
Toluene	Chlorobenzene (monochlorobenzene)
Ethylbenzene	2-Chlorotoluene
m&p-Xylene	4-Chlorotoluene
o-Xylene	1,2-Dichlorobenzene
Halogenated Aliphatics	1,3-Dichlorobenzene
Bromomethane (Methyl Bromide)	1,4-Dichlorobenzene
Carbon tetrachloride	1,2,3-Trichlorobenzene
Chloroethane	1,2,4-Trichlorobenzene
Chloromethane	1,3,5-Trichlorobenzene
1,2-Dibromo-3-chloropropane	**Monoaromatic Hydrocarbons**
1,2-Dibromoethane (ethylene dibromide, EDB)	n-Butylbenzene
Dibromomethane	tert-Butylbenzene
Dichlorodifluoromethane	Isopropylbenzene (Cumene)
1,1-Dichloroethane	4-Isopropyltoluene (p-Cymene)
1,2-Dichloroethane	n-Propylbenzene
1,1-Dichloroethene	sec-Butylbenzene
cis-1,2-Dichloroethene	Styrene
trans-1,2-Dichloroethene	1,2,4-Trimethylbenzene
Dichloromethane (methylene chloride)	1,3,5-Trimethylbenzene
1,2-Dichloropropane	**Ketones**
1,3-Dichloropropane	Acetone
1,1-Dichloropropene	2-Butanone (MEK)
cis-1,3-Dichloropropene	Methyl tert-butylether (MTBE)
trans-1,3-Dichloropropene	4-Methylpentan-2-one (MIBK)
Hexachlorobutadiene	**Trihalomethanes**
1,1,1,2-Tetrachloroethane	Bromodichloromethane
1,1,2,2-Tetrachloroethane	Bromoform (tribromomethane)
Tetrachloroethene (tetrachloroethylene)	Chloroform (Trichloromethane)
1,1,1-Trichloroethane	Dibromochloromethane
1,1,2-Trichloroethane	**Other VOC**
Trichloroethene (trichloroethylene)	Carbon disulphide
Trichlorofluoromethane	Naphthalene
1,2,3-Trichloropropane	
1,1,2-Trichlorotrifluoroethane (Freon 113)	
Vinyl chloride	

List of PAHs analysed

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo[a,h]anthracene
Anthracene	Fluoranthene
Benzo[a]anthracene	Fluorene
Benzo[a]pyrene	Indeno(1,2,3-c,d)pyrene
Benzo[b]fluoranthene + Benzo[j] fluoranthene	Naphthalene
Benzo[g,h,i]perylene	Phenanthrene
Benzo[k]fluoranthene	Pyrene

Appendix 5 - TCLP Results

	V µg/L	Cr µg/L	Mn µg/L	Fe µg/L	Co µg/L	Ni µg/L	Cu µg/L	Zn µg/L	As µg/L	Cd µg/L	Pb µg/L
DL	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**10**	**1**	**0.1**	**0.1**	**1**
Acetic Acid Leachates											
HP10 surface	23.1	7.8	1135.8	7551.4	27.4	20.4	130	323	8	1.6	19
HP10 15cm	23.5	7.5	1324.9	8549.1	27.3	20.5	140	95	8	0.5	6
HP10 30cm	23.4	8.3	1169.8	9080.9	24.7	20.4	130	90	8.9	0.4	10
HP10 45cm	23.8	8.7	1047.4	9062.1	24.2	18.4	130	119	8.5	0.3	14
HP20 Surface	30	15.7	1124.3	8494.3	33.9	27.4	250	4466	25.6	8	363
HP20 15cm	50.3	20.4	1894.9	10480.1	33	25.2	170	4813	30.6	7.2	541
HP 20 25cm	58.7	28.3	2111.65	11079.5	38.75	27.3	190	3746.5	36.55	6.8	238.5
HP24	24.9	12.8	940.2	10050.5	32	27.7	180	240	20.2	1	53
CG	39.9	8.7	1195.3	12346.7	34.1	22.0	157	57	10.7	0.1	6
Water Leachates											
HP10 Surface	9.3	1.3	282.0	1788.5	6.4	3.2	30.3	82.0	1.1	0.3	15.4
HP10 15cm	8.6	1.2	307.5	1852.8	6.6	2.9	28.9	21.0	0.9	0.1	3.9
HP10 30cm	8.4	1.3	222.9	1874.7	5.0	2.5	27.1	21.0	1.0	0.2	6.7
HP10 45cm	8.6	1.4	189.0	2058.1	4.7	2.4	26.6	24.0	1.0	0.2	10.1
HP20 Surface	9.5	3.4	308.4	2112.5	8.6	5.4	124.7	1481.0	4.8	3.7	156.9
HP20 15cm	16.85	4.25	574.9	2843.8	9.5	5.85	42.6	1806.5	5.6	3.75	236.8
HP20 25cm	21.5	6.8	797.4	3427.1	13.7	7.8	65.3	1458	5.8	3.6	237.3
HP24 Surface	11.2	2.9	222.2	2655.6	7.5	5	41.2	78	2.5	0.6	39.3
CG Surface	14.2	2.1	282.9	4408.7	8	3.7	21.5	22	1.2	0.2	3.1
Blanks											
Blank water	**0**	**0.1**	**0.3**	**3.4**	**0**	**0**	**0**	**0**	**0**	**0**	**1**
Blank Acetic	**0**	**0.5**	**0.2**	**10.1**	**0**	**2.4**	**0**	**22**	**0.2**	**0.7**	**1**